

AD-A086 740 ARMY MOBILITY EQUIPMENT RESEARCH AND DEVELOPMENT COMM--ETC F/G 21/4
GASOLINES AND ENGINE OILS: LITERATURE REVIEW, NEW LABORATORY OX--ETC(U)
MAR 80 M KOLOBIELSKI, F MCCALEB

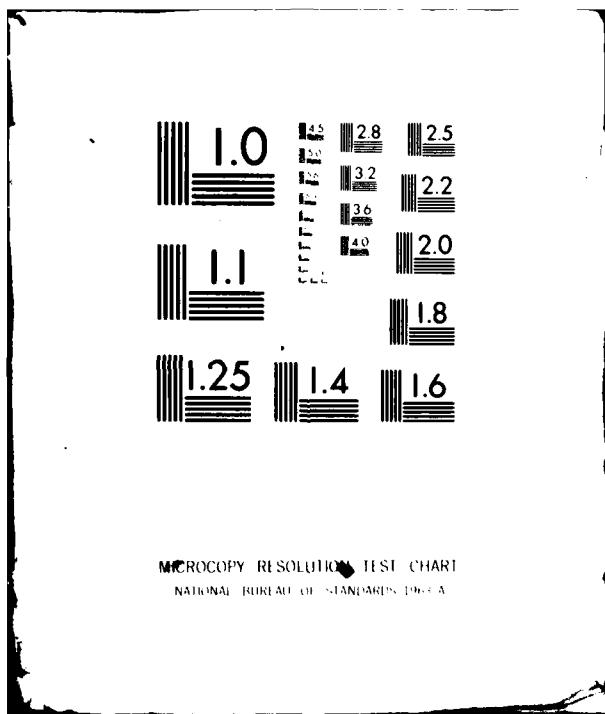
UNCLASSIFIED

MERADCOM-2296

NL

1 - 1
47-200-25-1

END -
DATE
FILED
8-80
DTIC



54
ADA 086740

LEVEL II
13

AD

Report 2296

GASOLINES AND ENGINE OILS: LITERATURE REVIEW, NEW
LABORATORY OXIDATION METHOD, AND SIGNIFICANCE
OF OLEFINS IN FUEL

by

Marjan Kolobielski

and

Fred McCaleb

DTIC
ELECTED
JUL 16 1980
S D

March 1980

A

Approved for public release; distribution unlimited.

U.S. ARMY MOBILITY EQUIPMENT
RESEARCH AND DEVELOPMENT COMMAND
FORT BELVOIR, VIRGINIA



80 7 14 036

**Destroy this report when no longer needed.
Do not return it to the originator.**

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM																				
1. REPORT NUMBER 2296	2. GOVT ACCESSION NO. <i>DD-A286 740</i>	3. RECIPIENT'S CATALOG NUMBER <i>NFM 100-2</i>																				
4. TITLE (and Subtitle) GASOLINES AND ENGINE OILS: LITERATURE REVIEW, NEW LABORATORY OXIDATION METHOD, AND SIGNIFICANCE OF OLEFINS IN FUEL.		5. TYPE OF REPORT & PERIOD COVERED Final																				
6. AUTHOR(s) Marjan Kolobielski and Fred McCaleb		7. CONTRACT OR GRANT NUMBER(s)																				
8. PERFORMING ORGANIZATION NAME AND ADDRESS DRDME-GL, Fuels and Lubricants Division; Energy and Water Resources Lab; US Army Mobility Equipment Research and Development Command; Fort Belvoir, VA 22060		9. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS																				
10. CONTROLLING OFFICE NAME AND ADDRESS US Army Mobility Equipment Research and Development Command; ATTN: DRDME-GL; Fort Belvoir, VA 22060		11. REPORT DATE March 1980																				
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 90																				
		14. SECURITY CLASS. (of this report) Unclassified																				
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE																				
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.																						
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)																						
18. SUPPLEMENTARY NOTES																						
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) (Continued on back) <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Base Oil</td> <td style="width: 33%;">Engine Oil</td> <td style="width: 33%;">Gums</td> <td style="width: 33%;">Oil</td> </tr> <tr> <td>Base Stock</td> <td>Engine Test</td> <td>Laboratory Test</td> <td>Olefins</td> </tr> <tr> <td>Correlation</td> <td>Field Performance</td> <td>Literature Review</td> <td>Oxidation</td> </tr> <tr> <td>Dielectric Constant</td> <td>Fuel</td> <td>Lubricating Oil</td> <td>Oxidative Stability</td> </tr> <tr> <td>Dipole Moment</td> <td>Gasoline</td> <td>Octane Number</td> <td>Oxygen Consumption</td> </tr> </table>			Base Oil	Engine Oil	Gums	Oil	Base Stock	Engine Test	Laboratory Test	Olefins	Correlation	Field Performance	Literature Review	Oxidation	Dielectric Constant	Fuel	Lubricating Oil	Oxidative Stability	Dipole Moment	Gasoline	Octane Number	Oxygen Consumption
Base Oil	Engine Oil	Gums	Oil																			
Base Stock	Engine Test	Laboratory Test	Olefins																			
Correlation	Field Performance	Literature Review	Oxidation																			
Dielectric Constant	Fuel	Lubricating Oil	Oxidative Stability																			
Dipole Moment	Gasoline	Octane Number	Oxygen Consumption																			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Review of literature on oxidation of gasolines and lubricating engine oils indicated shortcomings in present laboratory bench oxidation and engine tests. These tests are re-examined and their significance and some causes of poor precision are discussed. The newly developed laboratory oxidation method overcomes the shortcomings of the bench tests.																						
(Continued)																						

46-65

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

(Block 19. (Continued))

Polarization Index Refractive Index Re-refined Oil	Significance of Test Storage Stability	Precision Regression Equation	Specification Viscosity
--	---	----------------------------------	----------------------------

(Block 20. (Continued))

The new method consists of oxidizing a liquid sample in an autoclave under oxygen pressure at desired temperature for a determined period of time. A uniform and constant reaction temperature is maintained by stirring both the sample and the heating oil bath.

This method was applied to gasoline, its components, and contaminants and to engine oil and its base stocks. Two parameters are measured: oxygen consumption and Polarization Index (PI), an estimated increase of the dipole moment of the liquid product, determined from the dielectric constant (ϵ) and refractive index (n_D) ($PI = \epsilon - n_D^2$). A regression equation which includes these two parameters was developed for gasoline and engine oil. The new method has high repeatability and is a predictor of gasoline and engine oil oxidative stability.

Gasolines rich in reactive olefins were found prone to oxidation. It is predicted that in the future gasolines may contain high percentage of olefins, gum precursors, because of their high blending octane number.

Oxidative stability of formulated engine oil does not correlate with base stock oxidative stability or with the oil performance in engine and field tests. The lack of correlation is explained by the fact that the degradation of crankcase oil is caused by several factors, of which oxidation is only one.

PREFACE

The following persons assisted in this investigation:

Miss M. Adams - Infrared Spectra and Analyses.
Mr. P. A. Bennett - Reference Oil Samples.
Mr. J. Bowden - Fuel Samples and Analyses.
Mr. T. Bowen - Reference Oil Samples.
Mr. A. Coleman - Mass Spectroscopic Analysis.
Mr. E. Frame - Engine Oil Samples.
Mr. S. Levine - Analysis of Metals.
Mr. J. Reynolds - Re-refined Oil Samples.
Mr. J. Sonnenburg - Infrared Spectroscopic Analyses.

Accession For	
Internal	<input checked="" type="checkbox"/>
External	<input type="checkbox"/>
Unassigned	<input type="checkbox"/>
Classification	
By	
Classification	
Approved by Codes	
Entered by	
Entered or Special	

CONTENTS

Section	Title	Page
PREFACE		iii
ILLUSTRATIONS		vi
TABLES		vii
I INTRODUCTION		
1. Gasolines and Their Components		1
2. Lubricating Oils		1
3. Statement of Content		1
II REVIEW OF LITERATURE ON GASOLINE OXIDATION		
1. Effects of Gasoline Composition		2
2. Gum Precursors		2
3. Effects of Nitrogen Compounds		3
4. Reactivity of Hydrocarbons		3
5. Storage Stability of Gasoline-Gum Formation		3
6. Mechanism of Deposit and Gum Formation		4
7. Free Radical Oxidation Mechanism		4
8. Effects of Olefins		4
9. Conclusions of Gasoline Review		5
III REVIEW OF LITERATURE ON OIL OXIDATION		
1. Bench Tests		5
2. Single and Multicylinder Engine Tests (IIC and VC)		16
3. Sequence IIC Engine Test		17
4. Mechanism of Lubricant Action in Engine		18
5. Gas Turbine Engine Oil		20
6. Conclusions of Oil Review		20
IV RESULTS AND DISCUSSION: GASOLINE		
1. New Laboratory Oxidation Test – Techniques and Advantages		20
2. Polarization Index – New Oxidation Parameter		24
3. Correlation Between Two Measured Parameters		24
4. Oxidation of Model Compounds		25

CONTENTS (CONT'D)

Section	Title	Page
	5. Oxidation of Gasolines	25
	6. Deposit Formation upon Oxidation	25
	7. Significance of the Oxidation Test	29
	8. Olefins in Gasoline. Their Reactivity Evaluated by the Oxida- tion Test	29
	9. Olefins in Present Gasoline and in Gasoline of the Future – Effect on Storage Stability and Engine Operation	35
	10. Conclusions from Gasoline Study	37
V	RESULTS AND DISCUSSION: OILS	
	1. Oxidation Test: Conditions and Precision	37
	2. Test Parameters and Combined Results	38
	3. Oxidation Test on Synthetic Oils	38
	4. Relationship Between Oxidative Stability and Oil Characteristics	38
	5. Oxidation of Re-refined Oils	45
	6. Relationship Between Oil Oxidative Stability and Oil Perform- ance in Engine and Field Tests	50
	7. Conclusions from Oil Study	53
VI	EXPERIMENTS	
	1. Oxidation of Gasolines and Their Constituents – Apparatus and Procedure	55
	2. Oxidation of Oils	56
	LITERATURE CITED	57
	LIST OF SYMBOLS	73

ILLUSTRATIONS

Figure	Title	Page
1	Oxidation Apparatus	21
2	Oxidation Test on Gasolines	26
3	Oxidation of Olefins	32
4	Oxidation of Olefins	33
5	Oxidation of Olefins	34
6	Oxidation of Oils	43

TABLES

Table	Title	Page
1	Laboratory Oxidation Tests in Chronological Order	6
2	Laboratory Oxidation Tests – Test Conditions and Oxidation Parameters	12
3	Oxidation of Gasolines at 100°C and for 24 Hours: Effect of Reaction Conditions	22
4	Gasoline Oxidation: Tests Precision	23
5	Oxidation of Single Compounds – 10% Solution in Isooctane	27
6	Oxidation of Leaded Gasolines	27
7	Oxidation of Unleaded Gasolines	28
8	Oxidation of Olefins – 10% Solution in Isooctane	30
9	Examples of Olefins Present in Gasoline	36
10	Oil Oxidation. Test Precision	39
11	Oxidation of Oils	41
12	Oxidation of Synthetic Polar Oils	42
13	Oxidation of Model Compounds – Oil Components	44
14	Oxidation of Oils: Oxygen Consumption Versus Iodine Number	46
15	Viscosity Change of Oxidized Oil with Respect to Initial Product	47
16	Selected Dipole Moments and Viscosities	47
17	Oxidation of Oils – Water Content	47
18	Oxidation of Re-refined Base Stocks. Properties and Oxidative Stability	48

TABLES (CONT'D)

Table	Title	Page
19	Oxidation of Re-refined Oils: Base Stocks and Formulated Oils	49
20	Laboratory Oil Oxidation Test and Single-Cylinder Engine Test (L-38)	50
21	Laboratory Oil Oxidation Test and Engine Test-Sequence IIIC	51
22	Laboratory Oil Oxidation Test and Engine Test – Sequence VC	52
23	Laboratory Oil Oxidation Results and Field Performance	54

**GASOLINES AND ENGINE OILS:
LITERATURE REVIEW, NEW LABORATORY OXIDATION METHOD,
AND SIGNIFICANCE OF OLEFINS IN FUELS**

I. INTRODUCTION

The scope of this project includes oxidation studies on two types of products: gasolines and their components and engine lubricating oils and their base stocks.

1. Gasolines and Their Components. Military fuels, because of strategic considerations, are sometimes stored for five years and longer. Under such conditions, some components of gasoline undergo autoxidation reactions, producing small amounts of higher molecular weight compounds commonly called gums. The military services (1-8)* and industrial organizations (9-13) recognized that these gums are harmful to spark ignition engines. The existing empirical laboratory tests of accelerated aging are not satisfactory for predicting the stability of gasolines and their tendency to form gums in storage (14-20). The newly developed method overcomes these shortcomings.

2. Lubricating Oils. Lubricating oils were selected for this study because of military, environmental, and energy-saving needs.

The present Army specifications for engine lubricating oils require qualification and quality conformance tests (21). The quality conformance tests include only the measurements of physical properties. The qualification tests include, also, engine tests which evaluate certain performance characteristics of motor oils. In one of the engine tests, ASTM Sequence IIIC, it is assumed that oxidation of the oil is an important factor contributing to oil degradation (22). The engine tests are costly, and it would be advantageous for the Army to have simple techniques for use in qualification and quality conformance evaluation of motor oils. The new oxidation technique was applied to lubricating oils to correlate this bench method with the field and engine test performances.

In conjunction with the energy conservation and protection of the environment, the government is promoting a greater use of recycled or re-refined oil as base stock in the manufacturing of engine lubricating oils (23). The automotive engine oil is composed of a base oil, a hydrocarbon or ester-type compounds, and several additives.

* Numbers in parentheses refer to LITERATURE CITED, page 57.

In order to issue the proper specification for base oil it is necessary to know the effect of the oil on the performance of the final product - lubricating oil. Specifically, the effect of the composition of the base oil and the formulated oil on their oxidative stability was sought. This study clarifies some of the formulated oil - base oil relationships.

3. Statement of Content. This report reviews the state-of-the-art of oxidation of gasoline and lubricating oil and describes a newly developed laboratory method. The application of this method to various fuels, oils, and their components; the significance of the results; and a critical review of some presently accepted engine tests are presented. The importance of the effect of reactive olefins, which are components of current gasolines and projected to be used in the fuels of the future, is discussed.

II. REVIEW OF LITERATURE ON GASOLINE OXIDATION

Many studies were conducted on the autoxidation of hydrocarbons and gasoline as well as on storage stability of gasoline.

1. Effects of Gasoline Composition. In the forties, there were numerous studies on the effect of gasoline composition on the deposits formation in the engine. Aromatics, olefins, and some antioxidants were thought to cause the deposits (24) (25). It was found that traces of metal contaminants, mainly copper or copper salts, would act as oxidation catalysts and produce gum in storage (26). Recently, the specific catalytic activity of numerous alloys and metals, in the oxidation process of fuel, was determined and tabulated (27). Benson suggested that at low temperatures - below 150°C - the oxidation of most organic molecules will not proceed at a measurable rate without a catalyst or a radical initiation source (28). To prevent the undesirable oxidation, antioxidants (29-31) and metal deactivator additives were added to gasoline (30) (32). The chemistry of gum formation was studied and suggested that the components which contribute to gasoline instability are, in order of increasing effect: Paraffins, aromatics, monolefins, diolefins (33). Sulfur compounds were contributing also, while tetraethyllead did not have any effect (33).

2. Gum Precursors. Numerous symposia and conferences were organized to discuss the relationship between gasoline, engine malfunctions, and methods of testing. The consensus was that the gums which are formed during storage of gasoline by oxidation or otherwise are deposited in the induction system of the engine (11) (12) (34-36). The formation of gums was explained by the formation of oxygenated compounds-precursors, which by thermal condensation or polymerization give higher molecular weight products, less soluble and less volatile (37). The types of compounds

which contribute to gum formation, in a decreasing order, were: alkylbenzenes, cyclic olefins, sulfur compounds, polycyclic compounds, diolefins, and nitrogen compounds (19). It was claimed that sulfur, nitrogen, and oxygen compounds present in gasoline in concentrations of less than 1% were responsible for the formation of lacquer on the piston rings and gum deposits in the carburetor (38). However, there was no agreement on the relative contribution of different types of chemical compounds to gum formation. It was reported that olefins and mercaptans present in trace amounts in the fuel by co-oxidation reaction produce precursors of gums (39). Some have suggested that olefins and particularly conjugated olefins are highly reactive and are incorporated early in the gum formation process (40). In addition, the very methods of predicting gasoline stability were questioned with respect to their reliability (19). The oxidation rate of pure hydrocarbons was tabulated (41). The results indicate that olefins have a high rate of oxidation.

3. Effects of Nitrogen Compounds. Nitrogen compounds were singled out for studies as possible sources of gum. It was found that naphtha produced from shale oil and containing 1.2 percent nitrogen gave gums with an enriched content of nitrogen (8 percent) (42). Pyrroles, indoles, and pyridines were the main contaminants suspected of producing dark colored and black precipitates of petroleum fractions under storage (42-48). Early studies of the reaction mechanism explained the formation of the black deposit by oxidation of pyrroles and reaction with mercaptans (49). Later, it was shown that the pyrroles oxidation products include insoluble higher molecular weight 2-pyrrolone derivatives (50) and derivatives of maleimide (51). Upon storage, carboxylic acids accelerate the formation of sediments from fuel containing pyrrolic compounds (52).

4. Reactivity of Hydrocarbons. A review of oxidation of petroleum indicates the order of decreasing reactivity of hydrocarbons as: diolefins, aromatic olefins, olefins, aromatics, isoparaffins, naphthenes, and paraffins (20). Among aromatic hydrocarbons, cumene appears to be very reactive (53).

5. Storage Stability of Gasoline-Gum Formation. In numerous studies the researchers of the U.S. Bureau of Mines investigated the storage stability of gasoline. They found that after the removal of polar compounds containing nitrogen, oxygen, and sulfur, gasoline upon storage produced less gum than the original sample of fuel (54). The gum-forming reaction involved sulfur compounds, polycyclic hydrocarbons, and olefins (15) (55). Aromatic constituents of gasoline were responsible for significant formation of gum upon storage (15). Reactions between thioles and olefins were described as giving precipitates (16).

6. Mechanism of Deposit and Gum Formation. An alternate explanation of deposit formation in engine induction system has also been offered (56). Researchers have suggested that oxidation of amine compounds present in gasoline results in long chain amides and carboxylic acids. These compounds, being less soluble in gasoline, precipitate (56).

The mechanism of gum formation and fuel stability was studied at Stanford Research Institute. Gasoline was oxidized in the presence of ultraviolet light (57). The isolated gums were formed by reaction of thiols with olefins and also were derived from certain active nitrogen and sulfur compounds and from aromatics. Jet fuels were oxidized by heating at temperatures of 200° C; the deposit precursors included higher molecular weight aromatic compounds containing ester groups (58) (59).

Other investigators found that oxidation of jet fuel at higher temperatures gives dark deposits with higher sulfur content than found in parent fuel (60-62). Most susceptible to oxidation were indene, vinylcyclohexene, and octadiene (60) (63). Extensive work on the formation of deposits in jet fuels was conducted by Bolshakov (64). He found that increased oxidation was accompanied by an increase in the acidity of sediments.

7. Free Radical Oxidation Mechanism. The free radical chain mechanism applicable to gum formation during storage was presented by Mayo (65) (66) and reviewed by Polss (67). The mechanism of the slow oxidation reaction of hydrocarbons at low temperatures, below 200° C, was also reviewed (68) (69). In the first stage, the radicals are produced by thermal initiation without oxygen, thermal initiation with oxygen, or by decomposition of peroxidic oxidation products (65). After the radicals are generated, they can react in three ways, by oxidation, by polymerization and coupling, or by chain transfer. The coupling reaction increases the size of the initial molecules and might lead to gum formation. The activation energy of a number of elementary reactions which occur in the liquid phase during autoxidation of hydrocarbons has been determined (70). The reactivity was shown to be due to radical stabilization, steric effects, and polar factors (71).

8. Effects of Olefins. In more recent studies, reactive olefins present in the fuel are considered the most important components in the formation of gum in storage. Catalytically cracked gasoline, rich in olefins, was found to produce gums in storage (72-75). Also, naphtha, high in unsaturates, had a high gum content upon storage (76). Fuels containing olefins when exposed to an oxidative medium exhibit higher viscosity due to autoxidation and polymerization (77) (78).

It has been demonstrated that olefins react in the combustion chamber of a gasoline engine with nitrogen oxides to give nitro-nitrates derivatives which are transported as blow-by into the crankcase to give sludge by a further reaction (79). Therefore, it is suggested that the concentration of olefins in gasoline and their structure has an important effect on sludge formation.

9. Conclusions of Gasoline Review. At the conclusion of the literature review on gasoline oxidation, the following unanswered core questions remained: a reliable laboratory oxidation test and the identification of the specific olefinic compounds, gasoline components, which are responsible for the gum formation.

III. REVIEW OF LITERATURE ON OIL OXIDATION

In the early stages of automobile development, scientists and engineers assumed that oxidation of engine oil causes oil degradation and leads to engine malfunction. From the middle 1930's, oil additives containing oxidation inhibitors were used in lubricating oils (80). Currently with this practical solution, laboratory methods were developed to evaluate the resistance of engine lubricating oil to oxidation.

1. Bench Tests. One of the early methods used was the "Indiana Oxidation Test for Motor Oils" (81). It consisted of bubbling air through a 300-ml oil sample placed in a glass container and heating it in an oil bath at 172°C for several days. The amount of the sludge formed and increase in viscosity was measured to indicate the degree of oxidation. For the next 45 years many modifications of this basic bench test were developed. The laboratory oil oxidation tests conducted under atmospheric pressure are presented in Table 1, which includes a short description of each test and the significant results. Table 2 contains the tests classified according to specific test conditions and oxidation parameters.

Several laboratory oxidation tests were developed using rotary bombs under pressure at higher temperatures in order to prevent loss of the tested lubricant by evaporation (115-119). Performance of the oils were judged by measuring the induction period. The induction period is defined as the time required to reach certain concentration of a hydroperoxide or to absorb a definite amount of oxygen. Numerous review articles were published on engine lubricating oil requirements and oil oxidation tests (120-129).

This review of bench oxidation tests indicates that only one laboratory test has a good correlation with engine test. It was developed by Forbes and Wood (98). It is a potential predictor of oil performance in the engine used in the multi-cylinder Sequence V test. This bench test is a modification of a previously reported

Table 1. Laboratory Oxidation Tests in Chronological Order

Test Conditions	Measured Oxidation Parameters	Significant Results	Reference*
300 ml 172°C Oil bath air-bubbled several days.	Sludge Viscosity		81
95° to 175°C Fritted glass metal catalysts, several hours oxygen-bubbled.	Oxygen absorption Kinetics Oxidation products	Oxidation rate Varied with O ₂ flow rate.	82
125 ml 177°C Stirrer-3000 r/min copper bearings 6-10 hours.	Bearings corrosion	Correlation between corrosion of bearings determined in the lab and in the engine.	83
25°C Vessel shaken oxygen gas burette.	Oxygen absorption Kinetics		84
149°C Air-bubbled catalyst-Fe ₂ O ₃ soap 20 hours.	Viscosity Acid number		85
5g 125°C Static test catalyst-copper naphthenate oxygen	Induction time		86

Table 1. Laboratory Oxidation Tests in Chronological Order (Cont'd)

Test Conditions	Measured Oxidation Parameters	Significant Results	Reference*
150°C Oxygen	Induction time	Exponential regression equation between induction time and piston cleanliness.	87
250 ml 218°C Air-bubbled Catalyst-metal	Viscosity Neutralization number Sludge Metal Corrosion		88
5 g 125°C Oxygen Catalyst-ferric stearate Vessel shaken Removal of gaseous products	Induction time		89
Oil admixed with oxidized cracked naphtha $O_2 + N_2 + NO_2$ 93°C 5 hours.	Sludge	It is suggested that sludge in engine crank-case oil is formed from fuel combustion blow-by.	90
Oil admixed with combustion blow-by and H_2SO_4 93°C	Sludge		91
Oil film on a heated metallic drum admixed with blow-by	Sludge		92

Table 1. Laboratory Oxidation Tests in Chronological Order (Cont'd)

Test Conditions	Measured Oxidation Parameters	Significant Results	Reference*
100 g 110°C In copper cylinder 90 hours	Induction time Sludge Acid Number		93
30 g 120°C Oxygen-bubbled aluminum heating block catalyst: copper naphthenate iron naphthenate 164 hours	Sludge Acidity		94
40 ml 200°C Air-bubbled oil bath 6 hours	Viscosity Carbon residue CO band in IR	No valid correlation between various parameters.	95
Oil passed over spinning aluminum disk 260°-343°C	Deposit Oxygen consumption		96
100 ml 204°C Catalyst: copper 68 hours	Oil loss Sludge Corrosion		97
Oil admixed with oxidized cracked naphtha $O_2 + N_2 + NO_2$ 100°C	Sludge	Good correlation with sludge rating in sequence V test.	98

Table 1. Laboratory Oxidation Tests in Chronological Order (Cont'd)

Test Conditions	Measured Oxidation Parameters	Significant Results	Reference*
Dodecane oxygen 200°C	Kinetics Composition of oxidation product	Reaction rate dependent upon oxygen diffusion.	99
Octadecane 274°C	Composition of oxidation product		100
75 g 182°C Aluminum heating block oxygen-bubbled catalyst: Cu, Fe, Pb naphthenate	Viscosity acid number base number CO band in IR time to absorb 1200 ml O ₂	Correlation between absorption time and sulfur content of oil.	101
315°C Oxygen-bubbled aluminum heating block	Rate of oxygen absorption		102
200 ml 218°-274°C Aluminum heating block air-bubbled	Viscosity Sludge Acidity Corrosion		103
1 ml 160°C Oxygen	Time to absorb 5 ml oxygen		104
25 g 165°C Oxygen-bubbled catalyst-copper and iron wire 54 hours	Viscosity CO band in IR	No linear correlation with sequence III C test.	105

Table 1. Laboratory Oxidation Tests in Chronological Order (Cont'd)

Test Conditions	Measured Oxidation Parameters	Significant Results	Reference*
200 g 143° to 177°C $O_2 + NO_2$ streams Oil bath catalyst: Fe naphthenate or Fe and Cu Wire 177 hours	Viscosity Induction time	No linear correlation with sequence III C test.	106
260°C air-bubbled	Kinetics	Rate increased with increased air-oil interface.	107
0.5 ml Oxygen atmosphere Differential scanning calorimetry	Time to exothermic reaction		108
Base stock oxygen atmosphere 170°-230°C Diff. scanning calorimetry	Time to exothermic reaction		109
Oxygen at 500 lb/in ² Diff. scanning calorimetry	Time to exothermic reaction		110
Lubricant at 150°C Deposition tube at 330°C Air-bubbled	Deposit on hot tube	Linear correlation between deposit and antioxidant's concentration.	111

Table 1. Laboratory Oxidation Tests in Chronological Order (Cont'd)

Test Conditions	Measured Oxidation Parameters	Significant Results	Reference*
40 ml Oxygen-bubbled 230° to 255°C Copper and brass catalysts	Composition of oxidation product depletion of antioxidant		112
0.5 ml 60°C Oxygen + cyclohexane + azobisiso- butyronitrile	Induction time depletion of antioxidant	No linear correlation with viscosity increase in sequence III C test.	113
249°-540°C Air + hexadecane	Composition of oxidation product		114

* Numbers refer to LITERATURE CITED, page 57.

**Table 2. Laboratory Oxidation Tests – Test Conditions
and Oxidation Parameters**

Test Parameters	References*
Amount of Oil Sample	
Up to 1 ml	104, 108, 112, 113
1 to 40 ml	86, 89, 94, 95, 105
40 to 100 ml	93, 97, 101
100 to 300 ml	81, 83, 88, 103, 106
Spray	96
Oxidant	
Air	81, 83, 85, 88, 93, 95, 103, 107
Oxygen	70, 82, 84, 86, 89, 102, 104, 105, 108, 109, 112, 113
$O_2 + N_2 + NO_2$	90, 98
$O_2 + NO_2$	106
Oxidant Applied by	
Bubbling	81, 85, 90, 93
Atmospheric pressure	83, 84, 86, 89, 93, 94
Through fritted glass	82
Means of heating	
Oil bath	81, 82, 85, 89, 95, 106
Water bath	84

**Table 2. Laboratory Oxidation Tests – Test Conditions
and Oxidation Parameters (Cont'd)**

Test Parameters	References*
Aluminum block	88, 94, 101, 102, 103
Heated metallic drum	92
Copper cylinder	93
Spinning disk	96
Reaction Temperature	
25°C	84
25° to 100°C	90, 91, 98, 113
100° to 150°C	70, 82, 85, 86, 87, 93, 94, 106, 111
150° to 200°C	70, 81, 82, 83, 95, 106, 109
Above 200°C	70, 88, 96, 97, 100, 102, 107, 112, 114
Catalyst	
Metal	82, 83, 88, 97, 103, 105, 106 112
Soluble iron oxide soap	85
Soluble ferric stearate	89
Soluble metal naphthenates	86, 94, 101, 106
Sludge precursor	90, 91, 92

**Table 2. Laboratory Oxidation Tests – Test Conditions
and Oxidation Parameters (Cont'd)**

Test Parameters	References*
Reaction Time	
Up to 10 hours	82, 83, 90, 95
10 to 72 hours	85, 87, 93, 105
Beyond 3 days	81, 93
Time to absorb X ml of oxygen	101, 104
Method of Agitation	
Stirrer	83
Shaking	84, 89
Oxidation Parameter	
Viscosity	81, 85, 87, 88, 95
Amount of absorbed oxygen	82, 84, 96, 101, 103
Acid number	85, 88, 93, 101, 103
Infrared spectrum	95, 101
Kinetics	82, 99, 102, 107
Induction period	70, 86, 87, 93, 101, 106
Time to exothermic reaction	108, 109, 110

Table 2. Laboratory Oxidation Tests – Test Conditions
and Oxidation Parameters (Cont'd)

Test Parameters	References*
Differential scanning calorimeter	108, 109, 110
Depletion of antioxidant	112, 113
Composition of oxidized oil	82, 99, 100, 112, 114
Loss of oil	97
Amount of sludge	88, 90, 91, 92, 93, 96, 97, 98, 103
Deposit	111
Corrosion of metals	83, 88, 97, 103

* Numbers refer to LITERATURE CITED, page 57.

method (90). The original method considered the blow-by, derived from the fuel and its combustion product, an important factor affecting oil oxidation (90). Since the authors (98) presented only a regression line, we calculated the regression equation from the published data. The equation is:

$$\text{Sludge In Sequence V} = -14.44 + 0.71 \times \text{Merit Bench Rating}$$

where $n = 17$, correlation coefficient is 0.94, and standard error of estimate is 2.84. The engine sludge rating varied from 20 to 49.

Tables 1 and 2 indicate that no linear correlation was found between different laboratory bench tests and Sequence III engine test (105) (106) (113). Many of the above listed bench tests were adapted and further developed by different organizations despite lack of correlation with engine tests. These laboratory tests were finally adapted as standard methods by governmental agencies (130) (131) and technical societies (132) (133).

2. Single and Multicylinder Engine Tests (IIC and VC). In addition to bench tests, the evaluation of engine oil performance is conducted in single-cylinder and multicylinder engines as well as in field tests in actual vehicle service. The standard engine tests were published by government agencies (134), technical societies (22) (135) (136), and international organizations (137) (138). In many cases, different organizations published the same engine test. The ultimate objective of this project in the area of lubricating oil is to develop a laboratory oxidation test able to predict oil performance in engines; therefore, the significance of the known engine tests is being reexamined below. Two criteria are used: precision of the laboratory engine tests, and their correlation with field results. It has been noted that the engine test methods have not been subjected to the usual strict standardization procedure of ASTM (22) (135). In fact, the precision of most single engine tests is poor (FTM 348, FTM 340.2, FTM 346, and FTM 341.2) (135). The FTM 3405.1 test has coefficient of variation, which is too broad (13.7 percent to 38.5 percent) (135).

Among multicylinder engine tests, the Sequence VC method has a good precision for determining average sludge, average varnish and piston varnish parameters, under low speed, low temperature, stop-and-go driving, and moderate turnpike operation (22). No numerical data were published to show correlation with field tests. However, a regression line was presented and it indicates the relationship between the same parameters determined in the field taxicab service and the laboratory Sequence V (122). Since Sequence V correlates, as previously mentioned, with Forbes and Wood's bench test, the latter gives a potential simple laboratory technique to predict engine oil performance under above described field service conditions.

Another multicylinder engine test, Sequence IIIC, has a good precision of rust and corrosion determinations (22). These values correlate to some extent with those obtained in a field test and are presented in the form of a graphic curve (22).

3. Sequence IIIC Engine Test. As mentioned previously in this report, the engine test Sequence IIIC was of interest to us because it claims to indicate the tendency of the oil to oxidation (22). The precision of this method is poor with respect to viscosity change and wear ratings (22). No regression equation was published to show the correlation between the values of these parameters measured in the laboratory and those found in the field (22). The graphs, which were published, indicate only the same order of viscosity increase for three oils subjected to laboratory and field tests (22). Since the relationship between the laboratory method and field test is significant, it is discussed in detail below.

The oil viscosity presumed to be the important parameter measured in both tests. Viscosity increase indicates the "thickening" of the engine oil, an event which is harmful and may cause engine failure (139-142). It was claimed that the increase in viscosity of used engine oil is caused by oxidation and nitration of the oil (140). The infrared carbonyl and nitrate bands were presented as supporting evidence (140). We suggest that these bands could also originate from fuel components. Other researchers proved, as cited before, that olefins present in the fuel or formed from the fuel in the combustion chamber, react with nitrogen oxides to give nitro-nitrates derivatives, which are transported as blow-by into the crankcase oil (79) (142). These materials and their further reaction products give infrared bands similar to those reported in reference 140, and increase the viscosity of the oil (79). Other investigators did not find a linear relationship between infrared carbonyl absorbance of the oil and its viscosity increase, in a laboratory engine test (142) (143). The concentration of these fuel-derived products in the oil and their effect on viscosity increase will depend upon the composition of the fuel, combustion chamber temperature, and the gap between the piston rings and the cylinder wall of the engine (144). Some researchers reported that the laboratory engine test, Sequence IIIC, correlates with the field tests (141) (145) (146). This conclusion was based on experiment containing only three samples and, therefore, statistically not valid. Later, field fleet tests were conducted to find the relationship between the engine oil viscosity and engine performance (147) (148). It was concluded that the laboratory bench tests do not satisfactorily predict the viscosity changes of the oil in the field (147) (148).

It was reported that the volatility of the lubricating oil is an important factor contributing to the oil viscosity increase (142) (149) (150) (151) (152). Numerous investigators disclosed that the shearing stress of the polymeric viscosity index improver, an additive present in multiviscosity oils, and oxidation of this additive

during engine operation, contribute to viscosity changes of the crankcase oil (105) (153) (154). The effect of the mechanical condition of the car on the viscosity change was also emphasized (155) (156) (157) (171). In summary, viscosity change of crankcase oil, the presumed indicator of oil oxidation (22) (140) (141), in fact reflects several phenomena. These include, in addition to oil oxidation, evaporation of the volatile lubricant's components, shearing of oil additives, and blow-by from the combustion chamber into the crankcase. In the field service, in addition to the oil, important parameters are: the fuel, car, and driving conditions, all of which may vary greatly and are difficult to control. We conclude that the viscosity change is not a valid indicator to be used in the laboratory engine test and field experiment.

4. Mechanism of Lubricant Action in Engine. Many researchers investigated the chemical and physical processes which take place in the engine during its operation. The objective was to gain better understanding of the mechanism of oil degradation and its effect on engine performance. In the early studies, the ring sticking and formation of lacquer and varnish on the piston was explained as oxidation of the engine oil in the crankcase and deposition of the insoluble acidic oxidation products in the piston ring belt (87) (158) (159). In more systematic studies the investigators distinguished three processes taking place in the engine, depending upon the mode of operation of the vehicle (160) (161). These were: operation of the engine at low temperature during short trips, at moderately low temperature, and at high temperature under heavy loads. At low temperature, a sludge is formed in the crankcase from the blow-by containing soot, condensable fuel, and fuel oxidation and other reaction products (161-166). The blow-by, derived from the fuel in the combustion chamber, enters the crankcase oil through the clearance between the rings and the cylinder wall. This product may corrode bearings (161) (162). The crankcase soot or carbon is predominantly formed from the fuel (167-171). Under moderate temperature conditions, the products derived from incomplete combustion of the fuel and its oxidation by polymerization form varnish (161). The reactive intermediate oxidation products include peroxy-acids, hydroxyacids, esters, anhydrides, lactones, ketones, aldehydes, alcohols, and olefins (163). At high temperature operation - piston ring zone at 250°C and crankcase at 150°C - the oil film may be exposed to high temperature of the ring belt for 0.5 to 1 percent of the time (161). Under such conditions, a fast oxidation reaction of the lubricant occurs, leading to deposition of varnish on the piston (161). Many authors suggested that the piston varnish may also contain soot and carbon derived from the fuel (163-166) (168).

Some researches emphasized the role of sulfur in the formation of piston deposits (101) (172). Kreuz suggested that the fuel or lubricant gives by oxidation, a hydroperoxide which further reacts with sulfur dioxide present in the blow-by. The sulfates which are produced give aldehydes and ketones by cleavage reactions. These two, in turn, form resins by condensation (172).

A laboratory oxidation study at high temperature of a model compound, octadecane, one of lubricant's base oil components, suggested another mechanism of deposit formation (100). It consists of oxidation and scission of the molecule to bifunctional compounds, which could polymerize to varnish (100). The oxidation mechanism of mineral oil at intermediate temperatures (100°C-220°C) was studied by several authors, who presented the intermediate steps and rate constants (70) (173). It was reported that oils with high aromatic content have increased thermooxidative stability (174).

Numerous reviews of the mechanism of oil oxidation in the engine were published (175-178). Several symposia were organized on liquid lubricant technology with emphasis on oil oxidative stability (179-186). Lansdown reported that the overall rate of oil oxidation is controlled by the rate of replenishment of gaseous oxygen and that no bench test results can be extrapolated to field applications (179). He believes that the thickening of diesel engine lubricants in long distance high-speed road transport is caused by accumulation of insoluble material derived from combustion soot (179). Rounds and Hunstet stated that oil oxidation in the engine leads to varnish and sludge formation, which in turn causes ring sticking (180). Salomon believes that in a stagnant atmosphere without oxygen replenishment, the oxidation reaction is catalyzed by the volatile oxidation products which cannot escape (181). Furry found that base oils upon refinement became less resistant to oxidation because of removal of natural oxidation inhibitors (182). In contrast, Klaus recommends to remove all nonhydrocarbons and unsaturated hydrocarbons from base oils and then admix the remaining pure product with oxidation inhibitors to obtain better oxidative stability (183). Salomon suggests that the usually accepted method of measuring the volume of absorbed oxygen under laboratory test conditions does not correlate with actual service. The concentration and type of harmful oxidation products formed during test are more significant (184). Also, trace amounts of impurities are deleterious (183). The soluble metal naphthenate catalysts which are used in the bench tests are not present in the crankcase oil during actual service (184). Appledoorn suggests that the highly over-refined base stocks may still retain good antiwear property, depending upon the combination of hydrocarbons which are present (185). He recommends to use the acidity, viscosity, and sludge formed during the laboratory oxidation test as criteria to assess the resistance of the oil to oxidation (185). Smalheer (186) agrees with the previously cited mechanism of sludge and varnish formation, which was related to the mode of engine operation (161). No theoretical criteria are available to select the additive combination best suited for a given base stock; therefore, a trial and error method is used (186).

The role of nitrogen fixation reaction in the engine's combustion chamber, leading to nitrogen oxides and finally sludge formation, was suggested in 1930's (187-189). However, as mentioned previously in this review, the mechanism was unequivocally proved by Vinyard and Coran (79).

5. Gas Turbine Engine Oil. Gas turbine lubricants, in contrast to gasoline and diesel engine lubricants, do not become contaminated with the fuel byproducts during service (190) (191).

6. Conclusions of Oil Review. The oxidation of oil in gasoline and diesel engines is only one of many variables contributing to lubricant degradation. There is no linear correlation between the tendency of oil to oxidation and engine or vehicle field performance.

The Forbes and Wood's bench test is a simple laboratory technique having potential for predicting oil performance under low speed, low temperature, stop-and-go, and moderate turnpike driving conditions.

IV. RESULTS AND DISCUSSION: GASOLINE

The objective of this part of the study was to develop a reliable laboratory oxidation test for gasoline and to identify the main components of gasoline responsible for gum formation during storage. The new test, its advantages and application to gasoline and its components, is presented in this chapter. Also, the presence and role of olefins is discussed.

1. New Laboratory Oxidation Test – Technique and Advantages. The usual test for determining the oxidation stability of gasoline is the ASTM Test D525(14), which is also used for routine screening of antioxidant gasoline additives (67). The shortcomings of this static test are: a limited gas-liquid contact area and difficulties in measuring the induction period - an indicator of gasoline susceptibility to oxidation. In addition, there is no linear correlation between the induction period and storage stability of gasoline (17). These shortcomings were overcome by developing a new laboratory oxidation test which employs different techniques with easily measurable parameters.

These parameters are: volume of oxygen consumed and estimated dipole moment of the oxidized fuel. The techniques employed are: absence of catalysts, stirring the fuel in an autoclave at constant speed and temperature under oxygen pressure for a determined period of time, and using a stirred heating oil bath. After experimentation, the temperature of 100°C and 24 hours reaction time were selected as best conditions for producing an extensive and measurable oxidation reaction. We decided to prevent any contact between metallic surfaces and the tested fluid in order to avoid the catalytic effect of such surfaces. It is known that with time such surfaces change and, therefore, have a variable effect on the reaction, resulting in poor precision. Our procedure consisted of coating the inside of the autoclave with teflon and using a polycarbonate stirrer (Figure 1).

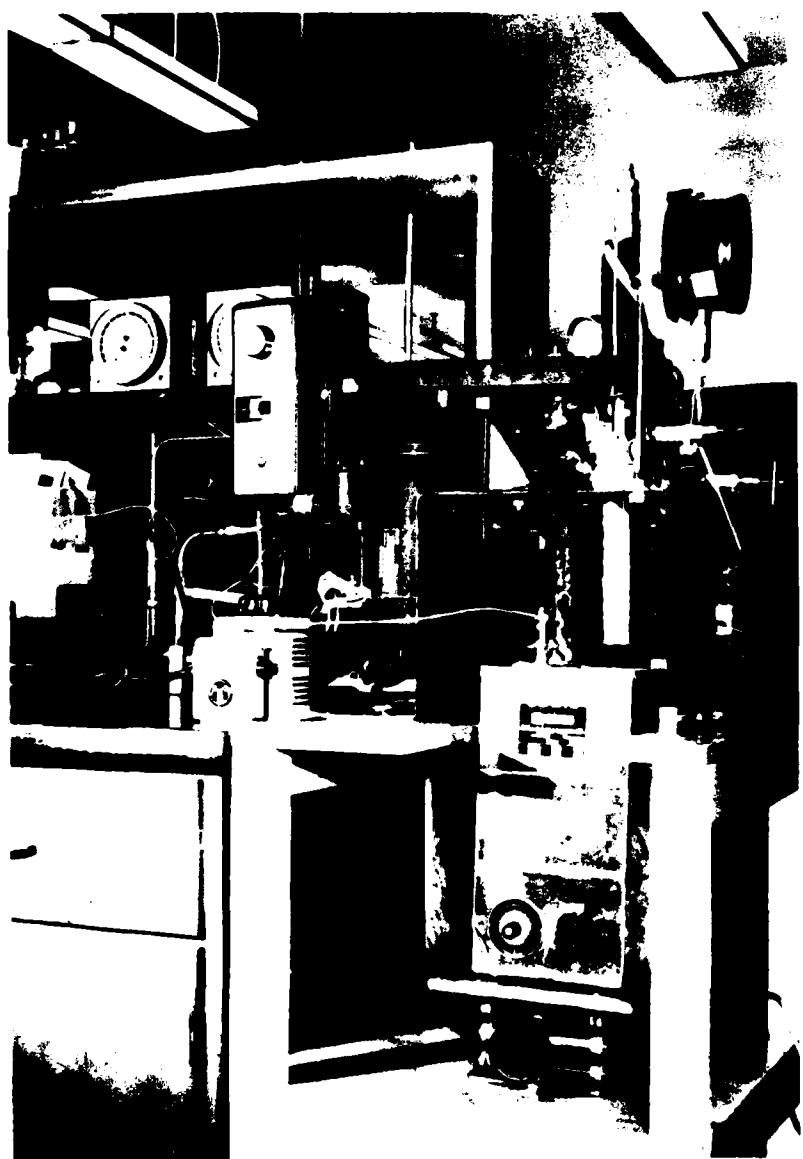


Figure 1. Oxidation apparatus.

The purpose of agitation during the oxidation reaction is to increase the contact area between the liquid and gas and to disperse the reaction heat, thereby preventing localized temperature increases (107) (192). This work revealed that a greater consumption of oxygen occurs during stirring than under the ASTM static conditions (Table 3, Tests 160-168 and 156-159, respectively). This finding suggests improved sensitivity of the new technique. The use of a stirred oil bath, instead of direct heating, further improved heat transfer and increased the precision of the procedures. The standard deviation of oxygen consumption in experiments with a heating mantle was 157 ml, while in the oil bath experiments, this was only 61 ml (Table 3, Tests 104-124 and 160-169, respectively). The new technique resulted in good repeatability of the test as shown in experiments with different gasolines (Table 4).

Table 3. Oxidation of Gasolines at 100°C and for 24 hours:
Effect of Reaction Conditions

Test No.	Sample No.	Reaction Conditions	Oxygen Consumption (OC) (ml)	Standard Deviation(S) (ml)
160	74	Agitation and oil bath	566	
162	74	Agitation and oil bath	522	
165	74	Agitation and oil bath	623	61
168	74	Agitation and oil bath	481	
159	74	ASTM static conditions	196	
156	74	ASTM static conditions	118	
124	73	Agitation and heating mantle	529	
126	73	Agitation and heating mantle	677	157
104	73	Agitation and heating mantle	842	

Table 4. Gasoline Oxidation: Tests Precision

Sample: AL-5894-G, Unleaded Gasoline

Test No.	Oxygen Consumption (OC), ml
778-48	1404
778-49	1363
778-50	1359
778-51	1370
778-52	1363

$\bar{X} = 1372 \text{ ml}$
 $S = 18.4 \text{ ml}$
 $V = 1.3\%$

Sample: Combat gasoline, APG (5/7/74)

Test No.	Oxygen Consumption (OC), ml
752-160	566
752-162	522
752-165	623
752-168	481

$\bar{X} = 548 \text{ ml}$
 $S = 61 \text{ ml}$
 $V = 11\%$

2. Polarization Index - New Oxidation Parameter. Gasoline, upon storage, undergoes autoxidation reaction. The final oxidation products are soluble polar compounds and insoluble products commonly called gums. Both have measurable dipole moments in contrast to the starting gasoline which is predominantly composed of non-polar hydrocarbons (193). In this method, the estimated increase in dipole moment was used as a criterion for predicting gasoline tendency to oxidation and formation of gums upon storage.

Under the reaction conditions, an excess of fuel with respect to oxygen was used: approximately 0.3 mole of gasoline per 0.07 mole of oxygen. Assuming that all oxygen was consumed, the reaction product represents a still dilute solution of polar compounds in a non-polar solvent. The Debye's method could have been applied to determine the dipole moment of the polar compounds (194). This procedure is too complicated to be considered for a routine test; therefore, an approximation method was developed. A non-polar substance has a dielectric constant (ϵ) roughly equal to the square of the refractive index (n_D^2), observed with visible light at the same temperature (195). It can be assumed that the difference ($\epsilon - n_D^2$) is an estimation of the dipole moment of a polar substance.

Other researchers have studied petroleum distillate oils containing polar sulfur compounds and found that fractions of high dipole moments had high values of the ($\epsilon - n_D^2$) expression (196). It also has been reported that this expression is in general agreement with the dipole moment of gasoline and its distillation fractions containing small amounts of polar substances (193).

This approach was further simplified by estimating the dipole moment of polar molecules present in the reaction mixture from the expression:

$$PI = \epsilon - n_D^2$$

where PI is named "Polarization Index," and ϵ and n_D are the dielectric constant and refractive index of gasoline. The PI values were established for the oxidized reaction product and for the starting material. The extent of oxidation was measured by Polarization Index Differential (PI_Δ) which was defined as the difference between the polarization indices of the two stages.

3. Correlation Between Two Measured Parameters. The validity of the new technique was confirmed by a highly significant correlation between PI and oxygen consumption (OC), measured independently in the experiments. The correlation was computed from the results of 46 tests. The regression equation is:

$$OC = 1517 PI_{\Delta} + 138$$

where the standard error of estimate is 129 ml, and the coefficient of correlation is 0.97 ($P < 0.001$, $n = 46$).

The results are presented in Figure 2. This equation indicates that with increased oxygen consumption there is an increase of the oxygenation reaction resulting in formation of polar oxygenated compounds at greater concentration. This formula provides a method for verifying the validity of each oxidation test by measuring the two parameters independently and comparing their values with the equation.

4. Oxidation of Model Compounds. In the first phase of this study, single compounds, gasoline components, or contaminants, were oxidized as 10 percent solutions in isoctane (Table 5). The pure solvent isoctane did not change significantly when treated with oxygen for a prolonged time. Under our reaction conditions, styrene was found to be susceptible to oxidation, as predicted by its reactivity (71).

5. Oxidation of Gasolines. Results of the oxidation tests on gasolines with known composition are presented in Tables 6 and 7. Most starting gasolines are not polar and have PI close to zero. The gasolines with relatively high olefin content are prone to oxidation and, as expected, gave high values of oxygen consumption and polarization index differential ($OC > 500$ ml and $PI_{\Delta} > 0.2$). It can be seen that gasolines high in aromatics and low in olefins are not susceptible to oxidation. The infrared spectra of the liquid reaction products confirmed the presence of polar molecules by showing strong CO and OH bands. In most of the advanced oxidation reactions, small amounts of solid or oily precipitates were formed (up to 0.7 g).

6. Deposit Formation Upon Oxidation. Several samples of combat gasoline, referee grade (MIL-G-46015), gave a dark deposit upon oxidation. The deposit contained greater amounts of nitrogen ($n = 0.11\%$) than the initial fuel. The fuel contained 28 percent aromatics 6 percent olefins, and 22 p/m of nitrogen. These results indicate the possible presence of traces of pyrrole compounds in the gasoline sample. Pyrrole compounds are producing dark colored precipitates when exposed to oxygen (49-51). In our experiments, a 10 percent solution of pyrrole in isoctane had also a high oxygen consumption and produced a large amount of black precipitate when oxidized for 24 hours. However, the nitrogen content of the deposit is still too low to indicate that the oxidation deposit is only formed by oxidative polymerization of pyrrole. Another mechanism of the deposit formation is advanced here. It suggests that gasolines containing pyrroles and olefins give, upon oxidation, carboxylic acids which react with pyrroles and oxygen to produce the deposits. The presence of carboxylic acids, in high concentration, in the deposits was confirmed by analysis. The reaction between pyrroles and acids in the presence of air, has been reported by other researchers (52).

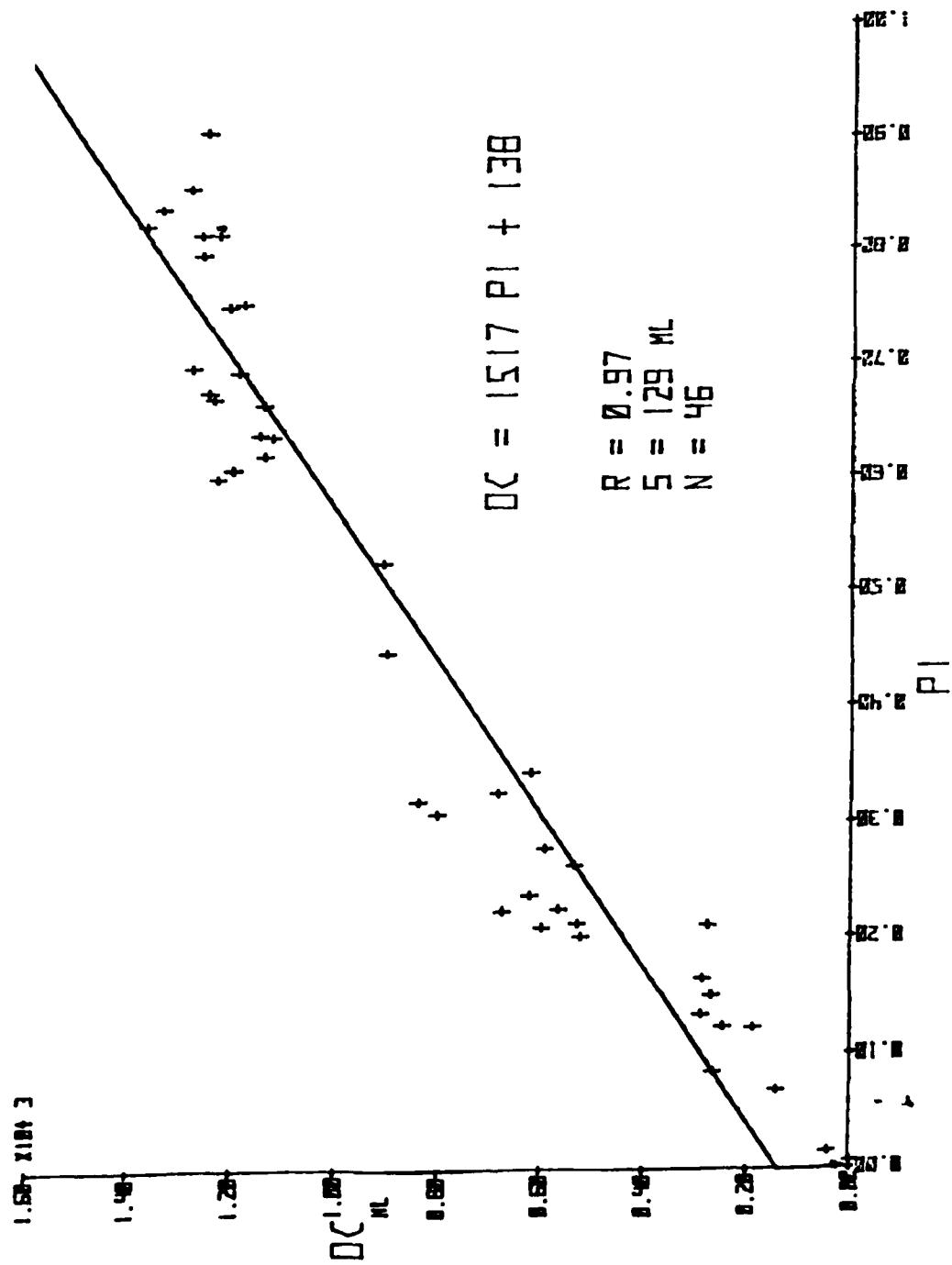


Figure 2. Oxidation test on gasolines.

Table 5. Oxidation of Single Compounds - 10% Solution in Isooctane

Starting Material	PI_Δ	OC, ml
Isooctane-Solvent	0.003	21
Cumene	0.007	0
m-Xylene	0.015	32
Secondary Butylbenzene	0.016	43
Di-t-Butylsulfide	-0.002	52
Di-t-Butyldisulfide	0.007	0
Styrene	0.250	882

Table 6. Oxidation of Leaded Gasolines

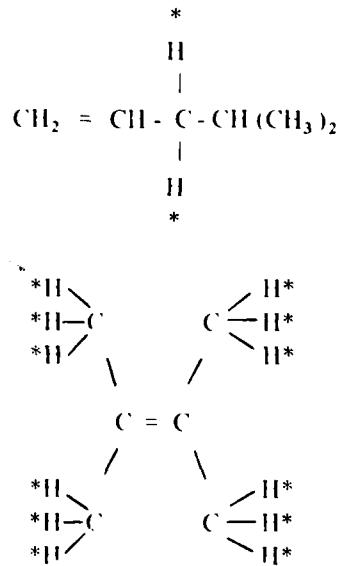
Composition of Gasoline Sample		PI_Δ	OC, ml
Aromatics, %	Olefins, %		
37	1	0.122	188
36	1	0.124	247
36	1	0.151	270
31	7	0.796	1264
24	7	0.635	1130
24	7	0.619	1145
20	9	0.752	1185

Table 7. Oxidation of Unleaded Gasolines

Composition of Gasoline Sample			
Aromatics, %	Olefins, %	PI _Δ	OC, ml
32	1	0.210	277
38	1	0.276	594
3	4	0.156	286
27	4	0.134	290
41	6	0.692	1196
41	6	0.750	1213
21	7	0.606	1204
21	7	0.599	1234
28	10	0.856	1288
36	12	0.663	1147
36	12	0.637	1155
29	19	0.906	1257
30	23	0.837	1344
30	23	0.823	1376

7. Significance of the Oxidation Test. This new oxidation test has a useful application in predicting storage stability of gasoline. It has been reported, using other accelerated oxidation tests, that a relationship exists between the amount of gum formed in ambient temperature storage and the volume of oxygen consumed by the fuel (55). The oxygen consumption and PI_Δ parameters can be assumed to indicate the susceptibility of gasoline to form gums in storage. These gums, as discussed above, may be harmful to engines. Gasolines with high OC and PI may produce engine failures. This was suggested by occurrences of spark plugs fouling in engines run on gasoline containing 6 percent of olefins and 41 percent of aromatics (Table 7). Also, problems occurred with the gasoline containing 12 percent of olefins and 36 percent of aromatics (Table 7). This was a development product manufactured from shale oil. It contained reactive dienes and deteriorated rapidly in storage. This fuel upon testing in engines caused heavy intake valves deposit and stuck valves.

8. Olefins in Gasoline. Their Reactivity Evaluated by the Oxidation Test. All the above results suggested that olefins present in gasoline have the greatest effect on the oxidation reaction and consequently on the storage stability of military fuels. However, it is known that different types of olefins, depending upon their structure, vary in their reactivity towards oxygen. In order to study the effect of structure in the extent of oxidation, as determined in this method, nine pure olefins were used. The compounds differ with respect to the number of allylic hydrogens as illustrated: 4-methyl-1-pentene having 2, while 2, 3-dimethyl-2-butene having 12.



These olefins, containing from 5 to 8 carbon atoms in the molecule, were oxidized as 10 percent by volume solutions in isoctane. The results are presented in Table 8.

Table 8. Oxidation of Olefins - 10% Solution in Isooctane

Olefin	Number of Allylic Hydrogens	OC, ml	PI_Δ	OC Adjusted for 0.1 Mole, ml
4-Methyl-1-Pentene	2	375	0.0575	964
2,3,3-Trimethyl-1-Butene	3	432	0.2003	1197
4-Methyl-2-Pentene	4	637	0.2115	1609
2-Methyl-1-Butene	5	640	0.2465	1382
2,4,4-Trimethyl-2-Pentene	6	768	0.3550	2259
2,4-Dimethyl-2-Pentene	7	914	0.4569	2608
2-Methyl-2-Butene	9	1316	0.6118	2794
2,3-Dimethyl-2-Pentene	11	1308	0.8490	3535
2,3-Dimethyl-2-Butene	12	1423	0.8909	3372
Isooctane Solvent		30	0	

A linear correlation was found between oxygen consumption and the number of allylic hydrogens (N):

$$\text{OC} = 111 \text{ N} + 141$$

where the standard error of estimate is 81 ml and the coefficient of correlation is 0.98 ($n=9$).

As expected, a linear regression equation was also found for PI_Δ and the number of allylic hydrogen atoms:

$$\text{PI}_\Delta = 0.0838 \text{ N} - 0.1180$$

where the standard error of estimate is 0.0112 and the coefficient of correlation is 0.99 ($n=9$). The two functions are presented in Figures 3 and 4.

The number of allylic hydrogen atoms is determined by the structure of the molecule of an olefinic compound; therefore, the oxidation data should compare equimolar amounts of the olefins. Consequently, the oxygen consumption was computed for 0.1 mole of each compound and the results are included in Table 8. The linear regression equation between OC adjusted for 0.1 mole and the number of allylic hydrogens is:

$$OC_{adj} = 264 N + 463$$

where the standard error of estimate is 240 ml and the coefficient of correlation is 0.97 ($n=9$).

The regression line is presented in Figure 5. The standard error is the adjusted standard deviation of the differences between the actual and the estimated values and amounts to $S = 240$ ml. The two lines are drawn in Figure 5 at 240 ml above and below the regression line. This is analogous to the practice in statistics of presenting the normal distribution curve, where the interval between the mean value minus one standard deviation and the mean value plus one standard deviation covers 2/3 (67 percent) of the population. In our graphical presentation (Figure 5) it can be seen that 67 percent of points (6 points) fell between these two lines or in zone with one standard error on either side of the regression line.

This finding has a practical application. It reduces the number of potentially harmful olefins present in gasoline, to those which are very reactive; those having high number of available allylic hydrogens. This new oxidation technique, combined with other simple analytical procedures may indicate the concentration and structure of an olefinic compound present in a gasoline sample. The other analytical procedures will include the separation by absorption chromatography of the olefinic fraction and the determination of iodine number and infrared spectroscopic analysis of this fraction.

The autoxidation of olefins is a free radical chain reaction involving several steps. This reaction has been studied by numerous investigators for many years. Their work has been focused on the mechanism of the reaction, determination of the yield of the hydroperoxides and the kinetics of the oxidation process with the rate constant determined for each step such as initiation, propagation, and termination reactions (197). It was reported that the behavior of unsaturated compounds towards oxygen was affected among others, by the availability of allylic hydrogens for the reaction with a peroxy radical (198). It was found in an oxidation reaction

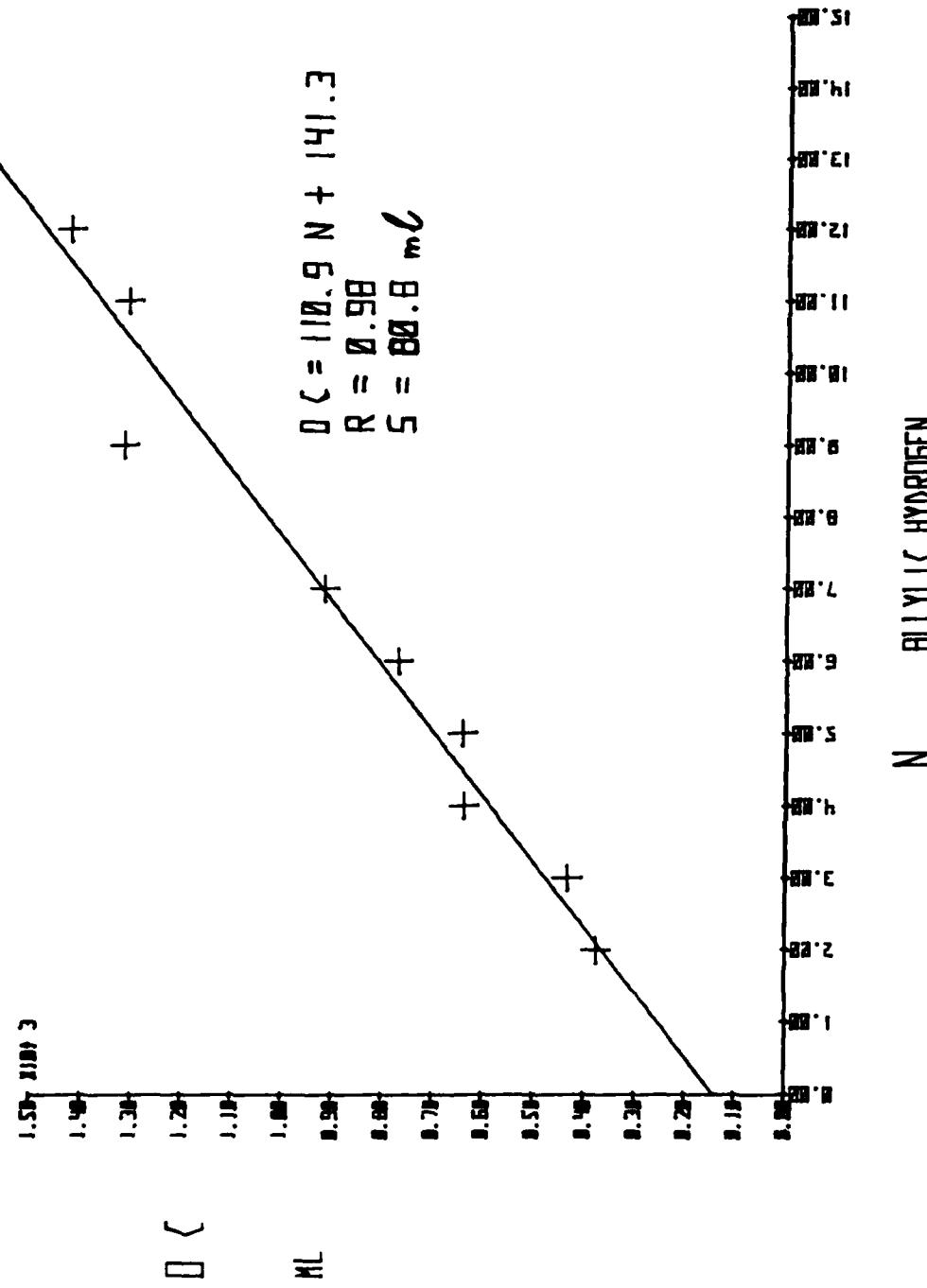


Figure 3. Oxidation of olefins.

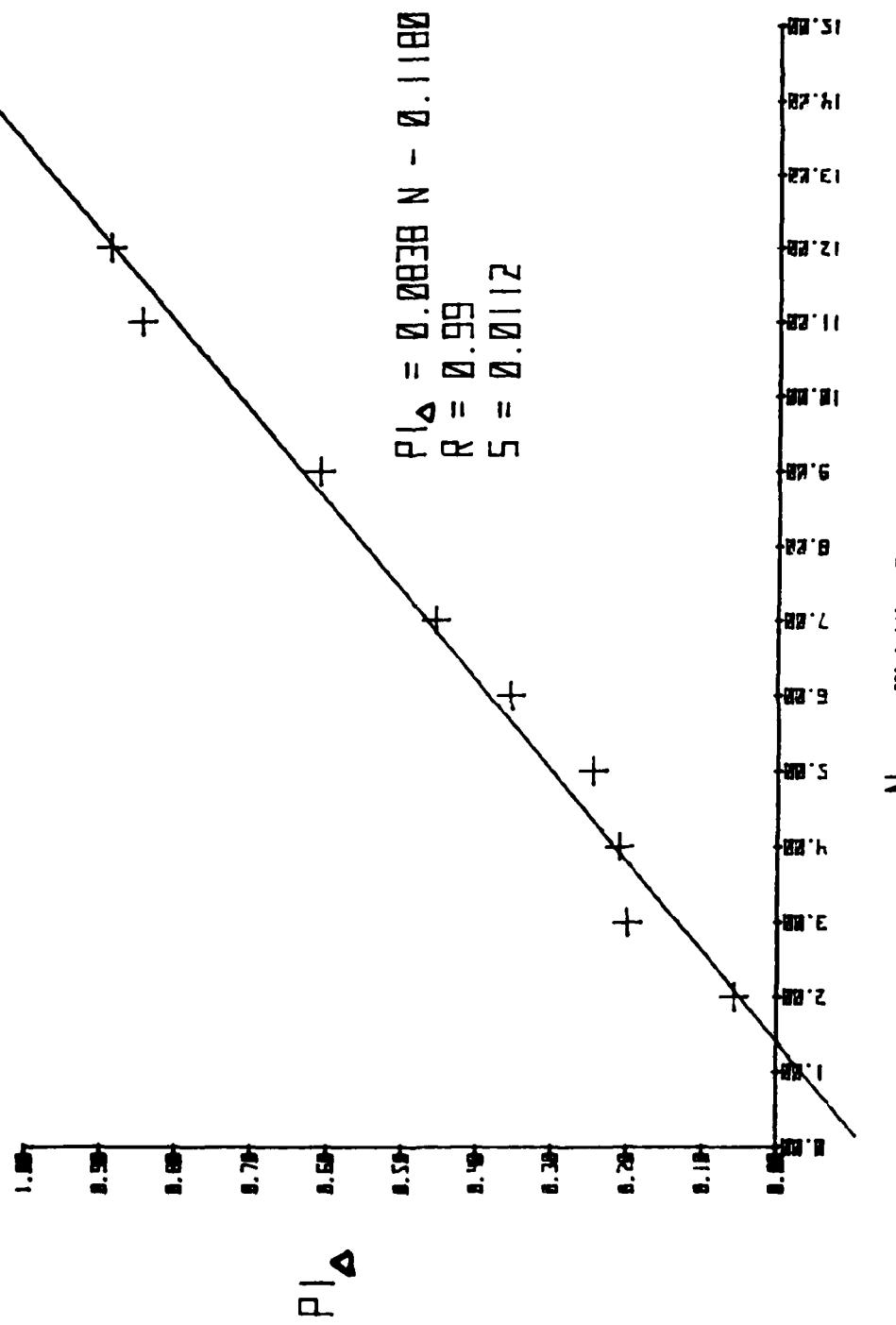
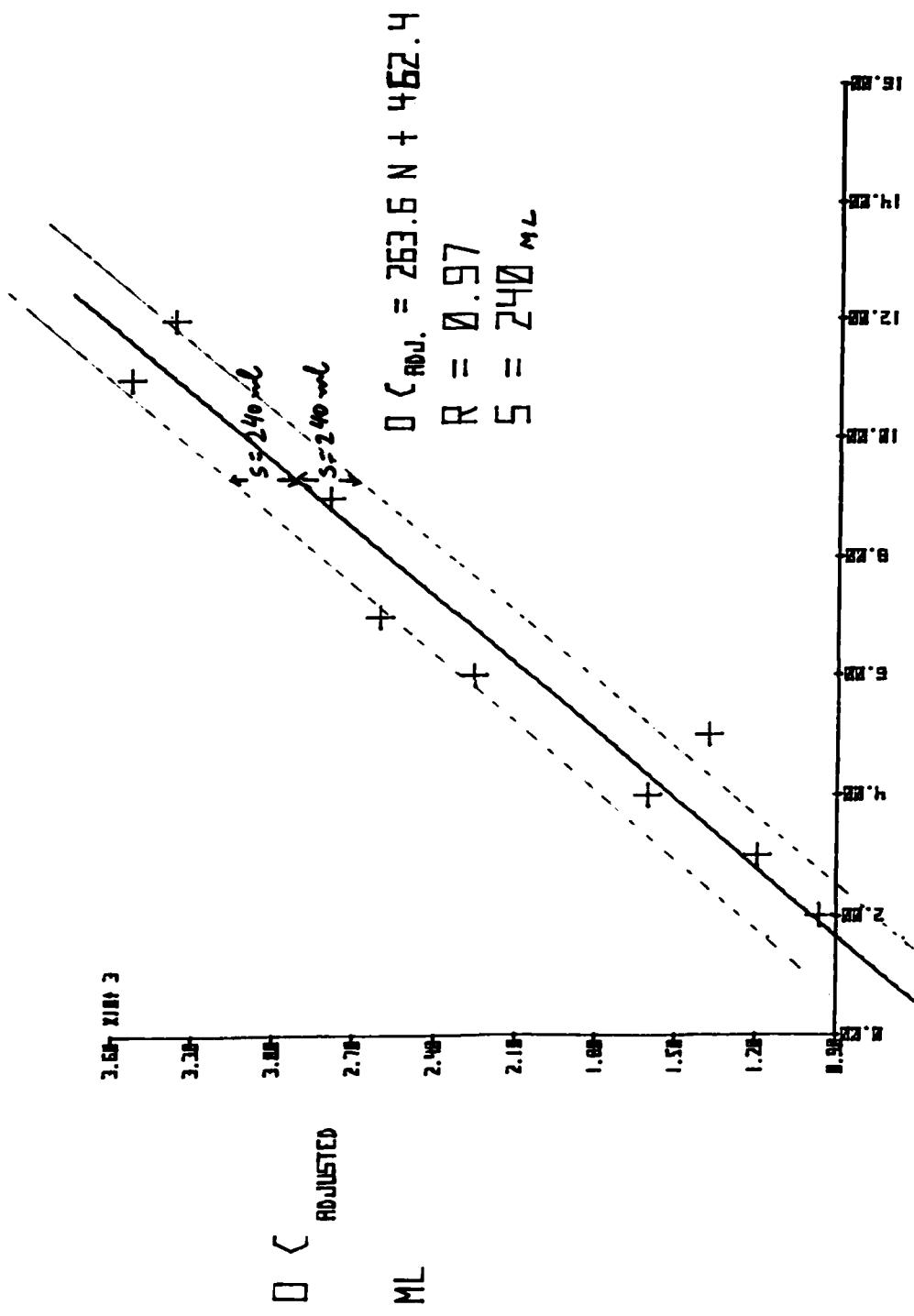


Figure 4. Oxidation of olefins.

N ALLYLIC HYDROGEN

Figure 5. Oxidation of olefins.



that 2-methyl-1-butene containing 5 allylic hydrogens was more reactive than 1-butene or 1-pentene with two allylic hydrogens (199). However, to our knowledge, no data have been reported on the simple linear relationship between the number of available allylic hydrogen atoms and the oxygen uptake or between this number and the concentration of the final oxygenated compounds as measured by their dipole moment.

If our finding could be extended to other olefins, it would provide a simple measure of the reactivity of olefins towards molecular oxygen, considering only the yield of the final oxygenated compounds such as alcohols, ketones, and acids.

9. Olefins in Present Gasoline and in Gasoline of the Future - Effect on Storage Stability and Engine Operation. The presence of reactive olefins in gasoline raises questions about their role, concentration, and future use in gasoline as well as expected effect on engines.

Petroleum refiners consider olefins an attractive component of gasoline because unsaturates have higher blending octane number than the analogous paraffins and are available from the refinery processes (75) (200-203). It was confirmed by a fleet test that gasolines containing high percentage of olefins have high Road Octane Number (204). Numerical values of blending Research Octane Number (RON) of unsaturates and saturates are, for example: 1-pentene - 118, versus pentane - 62; 2,4,4-trimethyl-1-pentene - 150, versus 2,4,4-trimethylpentane - 100 (200) (205). The higher octane number of olefins can be explained by the fact that these chemicals ignite at lower temperatures and extend the combustion of hydrocarbons in spark ignition engines (206).

The presence of olefins in marketable gasoline was reported in numerous publications (207-216). According to one survey, there was an increase of average olefins content, measured at the refineries from 6 percent to 8 percent in the period of 1973 to 1974 (212). Other surveys, containing larger numbers of samples, indicate that the average percentage of olefins remained unchanged during the period of 1976 to 1979 and amounted to 7 percent (214-216). The range of olefins content was recently reported to be 0 percent to 26 percent (216 a).

Examples of olefins present in gasoline are shown in Table 9 along with their blending research octane number, number of allylic hydrogens, and literature references. It can be seen that those with high octane number have high number of allylic hydrogens and will therefore produce gums when present in stored gasoline. We can expect an increased concentration of olefins and specifically reactive olefins in gasoline in the future.

Table 9. Examples of Olefins Present in Gasoline

Olefins	Number of Allylic Hydrogens	Blending RON	% in Gasoline	Reference
Isohexene	2	112	ND	202
Diisobutylene	5	148	ND	216 b
2-Pentene	5	150	0.9	208
2-Pentene	5	150	1.6	209
2-Heptene	5	94	ND	213
2-Octene	5	74	ND	213
Isobutylene	6	170	ND	216 b
2-ethyl-2-hexene	7	ND	ND	213
2-methyl-2-pentene	8	159	1.2	207
2-methyl-2-pentene	8	159	0.3	208
3-methyl-2-pentene	8	125	1.2	208
2-methyl-2-heptene	8	106	ND	213
2-methyl-2-butene	9	140	1.8	207
2-methyl-2-butene	9	140	1.0	209
2-methyl-2-butene	9	140	ND	213
2-methyl-2-butene	9	140	ND	216 b
2,3-Dimethyl-2-butene	12	185	0.1-0.2	207

Older cars and new cars with higher compression ratio require gasoline with higher octane number (217, 218). To increase the octane number and the yield of gasoline, the following refining processes will be emphasized in the future: polymer (200, 219-223) and pyrolysis gasoline manufacture (224-226), steam cracking (219, 227, 228), thermal cracking (229), catalytic cracking (230-238), and hydrocracking (239-241). The fuel from these processes, despite hydrogen treatment, will contain olefins because of the desired high octane number (217, 220, 223, 225, 226, 230, 231, 234, 237). Such gasoline in the future, and specifically the fuel containing olefins like isobutlenes (217) and isoamylenes (234), with high allylic hydrogen content, may produce gum in storage, despite treatment with antioxidant additives (201). Harm to the engines may result.

10. Conclusions from Gasoline Study.

- a. The new oxidation test is a reliable method for determining the oxidative stability of gasoline and its components.
- b. Gasoline containing olefins, and particularly reactive olefins, is prone to oxidation and formation of gum during prolonged storage.
- c. The susceptibility of olefins to oxidation correlates with the number of allylic hydrogen atoms in the molecule.
- d. Olefins prone to oxidation, as determined by this method are the components of present gasoline and the fuels of the future.
- e. Gasoline in the future may have lower storage stability and on storage form gum which will impair the operation of vehicles.

V. RESULTS AND DISCUSSION: OILS

The successful development of laboratory oxidation method for gasoline suggested its applications to engine oils. The objective was to develop a precise bench oxidation test which would correlate with engine tests and field performance. The knowledge of oxidative stability of base stocks and the effect of this stability on the formulated oils was also sought.

1. Oxidation Test: Conditions and Precision. The optimum reaction conditions which were determined experimentally consisted of stirring 50-ml oil sample at 350 r/min and 150°C for 48 hours. The initial pressure was 100 lbf/in². The precision of the method was high according to oxidation tests performed on several engine oil samples (Tables 10 and 12).

2. Test Parameters and Combined Results. As in the gasoline study, the extent of oil oxidation was ascertained by measuring independently oxygen consumption and polarization index differential. A significant correlation between these two variables was found based on 50 tests performed on nonpolar hydrocarbon oils. The regression equation is:

$$OC = 4751 PI_{\Delta} + 166$$

where the standard error of estimate is 155 ml, and the coefficient of correlation is 0.90 ($p < 0.001$, $n=50$).

This equation indicates that with increased oxidation, there is an increase of the dipole moment of the oil. Similar results were reported by other researchers (160). It provides a practical method for verifying the validity of each oxidation test by comparing the measured value of OC and PI_{Δ} with the equation. The oxidation results are presented in Table 11 and Figure 6. The oxygen consumption varied from 36 to 1532 ml and shows the ability of this test to discriminate oils of different oxidative stability.

3. Oxidation Test of Synthetic Oils. The Polarization Index formula ($PI = \epsilon - n_D^2$) cannot be applied to polar synthetic lubricating oils because they predominantly contain esters of high dipole moments. The polar molecules interact since they are not separated by nonpolar molecules of the liquid solvent. The measured PI values of bulk polar compounds therefore are not linearly related to the dipole moments of these materials. Our Polarization Index method is applicable to gasolines and oils with low initial dipole moments and which upon oxidation, still represent dilute solutions of polar molecules in a nonpolar solvent, hydrocarbon. The PI values of polar oils as measured in these experiments may only approximate the high polarity of these substances. The oxidation results on synthetic oils are presented in Table 12. The oxygen consumption was used as the only criterion. These oils are relatively resistant to oxidation. The coefficient of variation is relatively low, confirming the high precision of the oxidation method.

4. Relationship Between Oxidative Stability and Oil Characteristics. The purpose of this phase of our study was to gain better understanding of the effect of oil properties on the oxidative stability of the oil. These properties included chemical composition, unsaturation, viscosity, water content, concentration of elements-potential contaminants, gravity, and boiling range. Oxidation runs performed on a few model compounds-engine oil components did not show any increase of oxygen consumption or significant differences between the paraffinic, aromatic, and olefinic hydrocarbons of low reactivity (Table 13). These compounds were tested as 10- and 30-percent solutions in diester oil of high oxidative stability. Because of the polar character of the solvent, no polarization index was determined for these solutions.

Table 10. Oil Oxidation, Test Precision

Sample: Lubricating Oil, Synthetic Hydrocarbon, AL-5009 L.

OC ml	PI _Δ
674	0.1780
781	0.1510
713	0.1345
719	0.1359
686	0.1366
718	0.1328
690	0.1396
734	0.1457
712	0.1366
$\bar{X} = 714 \text{ ml}$	$\bar{X} = 0.1434$
S = 31 ml	S = 0.0142
V = 4.4%	V = 9.9%
n = 9	

Table 10. Oil Oxidation, Test Precision (Cont'd)

OC ml	PI _Δ
Sample: Lubricating Oil, AL-6193L, Formulated from Reprocessed Oil.	
320	0.0554
332	0.0554
319	0.0547
326	0.0562
322	0.0532
327	0.0569
$\bar{X} = 324 \text{ ml}$	$\bar{X} = 0.0053$
S = 5 ml	S = 0.0013
V = 1.5%	V = 2.3%
n = 6	

Table 11. Oxidation of Oils

Oil Sample		OC, ml	PI _A
No.	Description		
864	Rerefined Base Oil	381	0.0727
879	Rerefined Base Oil	811	0.0862
879	Rerefined Base Oil	882	0.0939
844	Rerefined Base Oil	496	0.0736
849	Rerefined Base Oil	493	0.0596
845	Rerefined Base Oil	515	0.0720
848	Rerefined Base Oil	889	0.1095
850	Rerefined Base Oil	451	0.0750
852	Rerefined Base Oil	482	0.0760
853	Rerefined Base Oil	511	0.0670
846	Rerefined Base Oil	807	0.1020
863	Rerefined Base Oil	427	0.0777
863	Rerefined Base Oil	459	0.1014
847	Rerefined Base Oil	702	0.0682
851	Rerefined Base Oil	482	0.0628
865	Rerefined Base Oil	459	0.0660
873	Rerefined Base Oil	612	0.0612
6755	Petroleum Base Oil	1498	0.2410
6755	Petroleum Base Oil	1502	0.2280
6850	Petroleum Base Oil	230	0.0624
1538	Rerefined Base Oil	256	0.0506
1539	Engine Oil Formulated from 1538	1002	0.1678
1526	Rerefined Base Oil	1532	0.3090
1527	Engine Oil Formulated from 1526	996	0.1498
6540	Engine Oil Formulated from Rerefined Oil	963	0.1059
6541	Engine Oil Formulated from Rerefined Oil	901	0.0997
6542	Engine Oil Formulated from Rerefined Oil	1077	0.1345
6	Engine Oil, Mil-L-2104 C	765	0.1237
3	Engine Oil, Mil-L-2104 C	617	0.0950
9	Engine Oil, Mil-L-2104 C	294	0.0454
4	Engine Oil, Mil-L-2104 C	309	0.0582
4	Engine Oil, Mil-L-2104 C	299	0.0485
2	Engine Oil, Mil-L-2104 C	954	0.1405
49	Engine Oil, Mil-L-2104 C	1503	0.1722
76	Engine Oil, Mil-L-2104 C	1014	0.1457
176	Reference Oil	612	0.0864
177	Reference Oil	761	0.1021

Table 11. Oxidation of Oils (Cont'd)

Oil Sample		OC, ml	PI_Δ
No.	Description		
178	Reference Oil	539	0.0721
70H	Reference Oil, Sequence Test IIC	1281	0.2427
70R	Reference Oil, Sequence Test IIC	1422	0.2733
72A	Reference Oil, Sequence Test IIC	622	0.0871
75A	Reference Oil, Sequence Test IIC	655	0.0831
75B	Reference Oil, Sequence Test IIC	1031	0.1656
75C	Reference Oil, Sequence Test IIC	690	0.1267
GT-A	Turbine Oil	246	0.0531
GT-B	Turbine Oil	36	0.044
GT-C	Turbine Oil	504	0.0655
GT-G	Turbine Oil	458	0.0823
GT-H	Turbine Oil	369	0.0349
GT-I	Turbine Oil	99	0.0149

Table 12. Oxidation of Synthetic Polar Oils

Sample	PI of Starting Material	Oxygen Consumption ml	S (%)
AI-5075	1.56	127	
AI-5075		144	11.3
AI-5075		115	
AI-5724	1.25	186	
AI-5724		213	
AI-5680	1.17	190	
AI-5680		203	9.6
AI-5680		229	

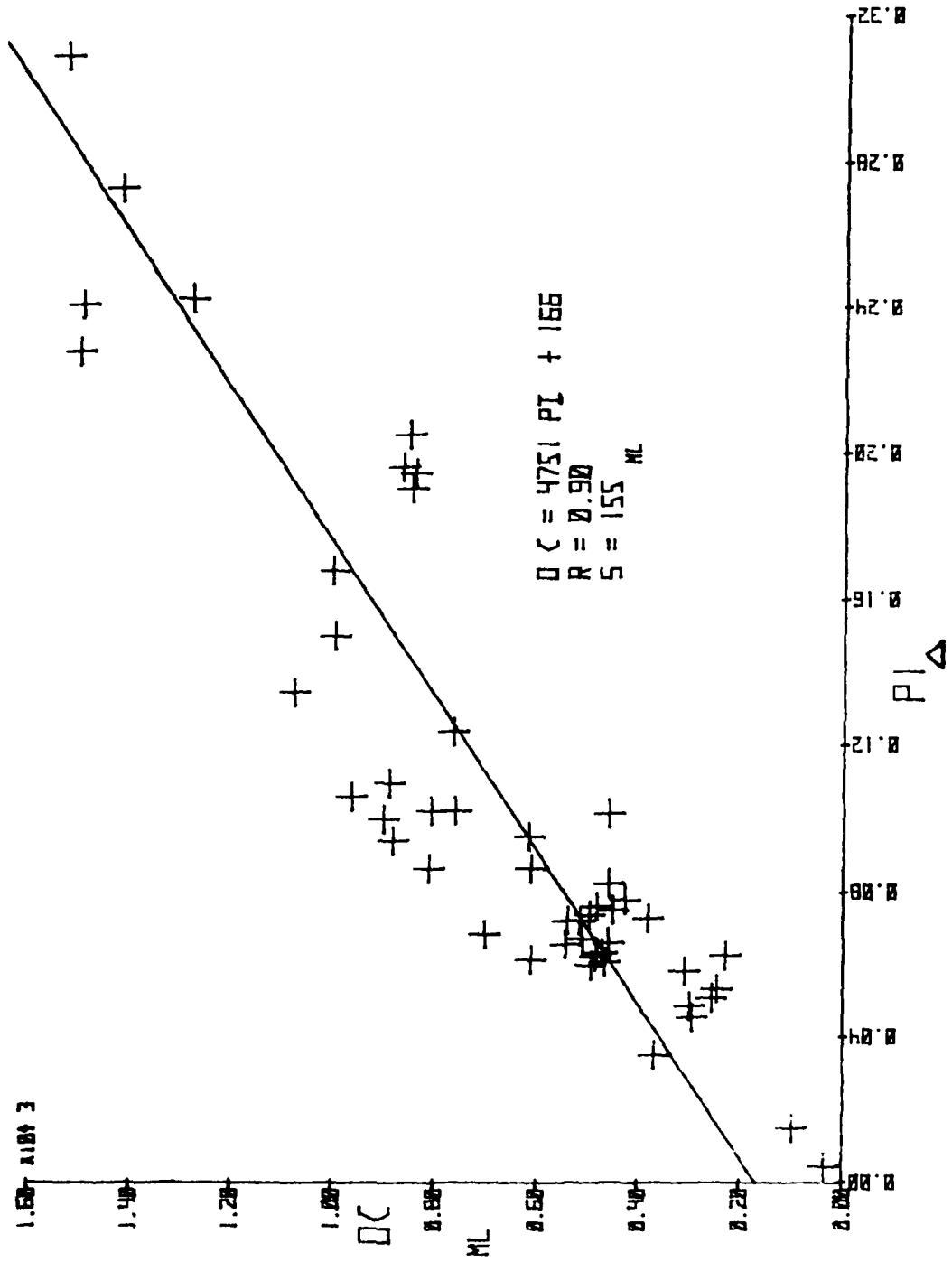


Figure 6. Oxidation of oils.

Table 13. Oxidation of Model Compounds - Oil Components

Solution in Diester Lubricant		
Compound		OC, ml
Solvent: Diester Oil, AL-5075		129 (average)
10% n Docosane		116
10% 1 Docosene		108
30% 1 Docosene		133
10% Dimethyl Naphthalene		161
10% Naphthalene		140
30% Tetradecane		144
30% Hexadecane		100

The quantitative determination of unsaturation of oils was performed by measuring iodine number of 28 samples. The results are presented in Table 14. The unsaturation was very low as indicated by low iodine number. No linear correlation was found between oxygen consumption and iodine number.

We cited in our literature review on oil oxidation (Section III, paragraph 3) some authors who reported that extended oil oxidation resulted in increased viscosity (140). No such linear correlation was found in our experiments when oxygen consumption and polarization index were compared with viscosity change after oxidation tests (Table 15). Such lack of correlation was expected. The value of the dipole moment of the oxidized oil depends upon the type and concentration of the oxygenated compounds, such as alcohols, aldehydes, ketones, and acids in the nonpolar hydrocarbon medium. Dipole moments and viscosities of several oxygenated compounds are presented as an example in Table 16. It can be seen that dipole moment does not correlate with viscosity. The high viscosity of the oxygenated compounds derived from the same hydrocarbon can be explained by the presence of intermolecular hydrogen bonding in the less polar compounds. Alcohols have higher viscosities than the corresponding aldehydes.

Water present in the oil because of high dielectric constant could affect the precision of our polarization index measurements. Also, water could affect the oil sample tendency to oxidation. Two oil samples selected randomly contained very low amounts of water before and after the oxidation test (Table 17). The Karl Fisher method was used. Such low concentration did not have a significant effect on the results. The effect of other characteristics of oil on oxidation is discussed in the following paragraph.

5. Oxidation of Re-refined Oils. In conjunction with Army-Environmental Protection Agency program on re-refined oils, a number of re-refined base stocks and finished engine oils made from these stocks became available (242). We investigated the effect of base stocks composition and characteristics on their oxidative stability and compared the latter with that of finished engine oils. The analyses of these oils were performed by other researchers (242). Table 18 contains a reproduction of these results along with our oxygen consumption data. It can be seen that no one property of the re-refined base stock correlates with its oxidative stability as measured by our test. Also, the aromatic content of these base oils (242) does not relate to their tendency to oxidation. The oxidation data on these oils are compared with those of corresponding finished lubricating oils (Table 19). In six cases, the formulated oils despite the presence of antioxidant additives were more susceptible to oxidation than the base stocks. In two, cases, no significant change was found, and in only one case, an improvement was observed. This finding suggests that the difference in oxidative stability of base stock has no effect on the properties of the

Table 14. Oxidation of Oils: Oxygen Consumption Versus Iodine Number

Oil Sample	OC, ml	Iodine Number of Starting Oil
AL-6193	324 (average)	4.65
AL-5009	714 (average)	3.66
CCL-864	381	4.60
CCL-879	846 (average)	3.37
CCL-844	496	4.74
CCL-849	493	4.78
CCL-845	515	4.75
AL-6755	1500 (average)	3.30
CCL-848	889	5.38
CCL-850	451	3.73
CCL-852	482	4.12
CCL-853	511	4.49
CCL-846	807	4.91
CCL-863	443 (average)	3.91
AL-6540	963	5.40
AL-6541	901	4.95
AL-6542	1077	5.12
AL-6850	230	3.60
ERDA 1538	256	3.70
ERDA 1539	1002	4.79
ERDA 1526	1532	4.60
ERDA 1527	996	4.63
ASTM GT-B	36	1.34
ASTM GT-A	246	3.78
CCL-847	702	5.12
Reference Oil 70R	1422	5.20
Reference Oil 70H	1281	5.41
Reference Oil LZ-1	1038 (average)	4.87

Table 15. Viscosity Change of Oxidized Oil with Respect to Initial Product

Oil Sample	OC, ml	Π_{Δ}	% Kinematic Viscosity Change at 100°F
Reference Oil, 70R	1422	0.2733	16.0
(MIL-L-2104C) 3	617	0.950	11.0
(MIL-L-2104C) 4	299	0.0485	-17.0
Reference Oil, LZ-1	1038	0.1662	38.0

Table 16. Selected Dipole Moments and Viscosities

Compound	Dipole Moment Debyes	Dynamic Viscosity Centipoise, at 20°C
Ethanol	1.65	1.2
Acetaldehyde	2.69	0.22
1-Propanal	1.68	2.26
Propanal	2.52	0.41
Cyclohexane	0.0	1.02
Cyclohexanol	1.69	68
Cyclohexanone	2.75	21
Toluene	0.36	0.59
Benzyl Alcohol	1.71	5.8
Benzaldehyde	2.75	1.39

Table 17. Oxidation of Oils Water Content

Oil Sample	OC, ml	% Water Content	
		In Starting Oil	In Oxidized Oil
AL 6755	1500	0.033	0.015
CCL 848	889	0.029	0.011

Table 18. Oxidation of Re-Reined Base Stocks. Properties and Oxidative Stability.

Sample Number Project		H11	H15	H16	H17	H18	H19	H20	H21	H22	H23	H24	H25	H26	H27	H28	H29	V.R.O.
K. Viscosity	ASTM No. D445	63.02	50.31	64.66	70.23	70.90	88.52	58.93	60.50	67.06	76.93	50.64	119.40	50.75	80.26	45.67	46.46	
@ 100°F, cSt		8.36	7.23	8.02	8.75	8.81	10.13	7.86	7.92	8.34	9.23	6.84	12.09	6.83	9.33	6.53	6.59	
@ 210°F, cSt		11.0	11.6	9.8	10.5	10.4	10.1	10.8	10.5	10.3	9.8	9.9	9.7	10.0	11.0	10.8		
Viscosity Index	D2270	20	20	20	20	20	30	20	20	20	20	20	20	20	20	20	20	
SAE Grade,*	D287	29.7	30.4	29.1	29.6	29.4	29.1	30.0	30.3	30.6	29.3	29.1	28.7	29.6	28.8	28.8	31.6	
AM Gravity,*	D1500	4.5	4.3	5.3	5.3	7.0	4.5	4.5	2.5	3.5	3.5	2.5	2.5	2.5	6.0	6.3	6.5	
ASTM Color	D524	0.14	0.13	0.13	0.09	0.15	0.24	0.06	0.05	0.05	0.08	0.06	0.10	0.06	0.14	0.34	0.07	
Carbon Residue, wt %	D97	-15	10	5	10	-23	10	15	5	10	10	15	15	15	15	-5		
Pour Point, °F	D92	4.25	3.80	4.25	4.10	4.40	4.30	3.85	4.15	4.15	4.40	4.65	4.50	4.35	3.65	4.0		
Flash Point, °F	D611	22.2	22.1	22.5	22.5	22.6	22.2	22.5	22.5	22.7	22.0	24.2	22.1	22.5	20.7	22.8		
Aniline Point,*°F	D644	0.09	0.16	0.16	0.05	0.11	0.22	0.05	0.17	0.10	0.08	0.04	0.04	0.09	0.11	0.17	0.03	
TAN	TBN	D2894	0.90	0.06	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.16
Copper Cor., 3hr @ 212°F	D130	1B	1B	1B	1B	1B	1B	1B	1B	1B	1B	1B	1B	1B	1B	1B	1A	
Chlorine, ppm	XRF	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	
Sulfur, wt %	XRF	0.21	0.16	0.31	0.18	0.14	0.19	0.14	0.16	0.16	0.12	0.15	0.16	0.14	0.15	0.24	0.39	
Phosphorus, ppm	D1091	7	24	3	25	65	23	30	33	5	17	14	9	5	5	7		
Elemental, ppm	MOD																	
Calcium	AA	10	<1	10	<1	10	11	10	<1	15	<1	44	<1	16	<1	16	1A	
Barium	AA	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	
Zinc	AA	<2	1.5	<2	<2	<2	11	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	
Lead	AA	<1	<1	<1	<1	<1	47	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	
Magnesium	AA	<1	1.2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	
Copper	AA	<3	<3	<5	<3	<5	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	
Chromium	AA	<5	<5	<3	<3	<5	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3	
Iron	AA	6	1.3	<2	<2	1.3	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	
Sodium	AA	<2	<2	<2	<2	<2	9	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	
Silicon	AA	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	
Aluminum	AA	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30	
Saponification No.	D94	0.43	0.37	0.49	0.36	0.52	0.7	0.35	0.39	0.24	0.21	0.25	0.22	0.38	0.43	4.1	ND	
Total Ash, wt %	D482	<0.001	0.014	<0.001	<0.001	0.036	0.004	<0.001	0.005	0.003	0.009	0.001	0.004	0.001	0.022	0.004	ND	
Nitrogen, wt %	PE	0.03	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	
Oxygen, wt %	PE	0.66	0.51	0.70	0.80	0.76	0.81	0.65	0.53	0.41	0.55	0.55	0.55	0.55	0.55	0.68	0.44	
Benzene Insolubles (unconjugated), wt %	D893	0.032	0.016	0.014	0.013	0.022	0.018	0.013	0.022	0.012	0.016	0.017	0.020	0.026	0.024	0.030	0.016	
CC BP Distribution % Off @ °C	1	224	295	346	330	298	346	240	257	216	314	337	335	338	270	226	383	
	5	370	366	377	383	366	382	339	371	383	380	397	380	368	326	400		
	10	388	384	394	403	390	405	377	388	390	400	395	414	397	357	414		
	50	444	441	448	466	455	465	442	443	447	452	450	483	453	434	450		
	90	535	545	540	574	537	563	539	539	532	518	600	518	564	555	488		
	Residue, wt % @ 600°C	5	5	6	3	5	4	1	<1	10	<1	5	5	5	5	5	5	
Inherent Consumption, ml	1000	145	147	147	147	147	147	147	147	147	147	147	147	147	147	147	147	

AA = Atomic Absorption.

ND = Not Determined.

PE = Petrol Ester.

V.R.O. = Viscous Residue.

Table 19. Oxidation of Re-Refined Oils: Base Stocks and Formulated Oils

Oil Sample	OC, ml	PI_{Δ}
Base Stock 846	807	0.1020
Formulated, OS-37708	846	0.1343
Base Stock 848	889	0.1095
Formulated, OS-37606	1317	0.2239
Base Stock 850	451	0.0750
Formulated, OS-37709	885	0.0963
Base Stock 852	482	0.0760
Formulated, OS-37710	775	0.1259
Base Stock 853	511	0.0670
Formulated, OS-37711	757	0.1208
Base Stock 863	443	0.0895
Formulated, OS-37607	867	0.1433
ERDA Re-refined Base Oil 1538	256	0.0506
Formulated, 1539	1002	0.1678
ERDA Re-refined Base Oil 1526	1532	0.3090
Formulated, 1527	996	0.1498
Base Stock AL-4598	421 (average)	0.0733 (average)
Formulated, AL-4597	425 (average)	0.0754 (average)

formulated oil. Other researchers have found that the differences in base stock can be adequately compensated for by changes in type and concentration of additive (243) (244). No relationship was reported between base stock characteristics and the performance of engine oil formulated from such stock (186) (245). We conclude, in agreement with our literature review, that the oxidative stability of the engine oil is not a primary factor in oil performance. This conclusion is confirmed by engine and field tests described in the following paragraph.

6. Relationship Between Oil Oxidative Stability and Oil Performance in Engine and Field Tests. Engine oil samples were received from the same investigators who published the engine and field test results. No correlation was found between oxygen consumption in our test and performance in single-cylinder engine test (L-38, FTM 3405.1) (Table 20).

Table 20. Laboratory Oil Oxidation Test and Single-Cylinder Engine Test (L-38)

Oil Sample	OC, ml	L-38 Test
REO 176	612	Satisfactory performance
REO 177	761	Failed
REO 178	5.39	Failed
AL-4597	425 (average)	Satisfactory performance

Thirty-four engine oils of known performance in Sequence IIIC engine test were evaluated by our oxidation method (Table 21). The first nine products on the list were formulated from previously described re-refined base stocks (242, 246). No linear correlation was found between oxidative stability of engine oils and the parameters which are determined in this engine test. These parameters include viscosity increase at 40 and 64 hours and ring land deposit. This laboratory finding confirms our previous conclusion based on literature data that viscosity change in Sequence IIIC is a poor predictor of crankcase oil action and that the Sequence IIIC is not related to field performance.

This oxidation test was also applied to 21 engine oils of known performance in Sequence VC engine test (Table 22). No linear correlation was found between oxygen consumption and parameters such as piston varnish, average engine varnish and average sludge, all of which are usually determined in this engine test. As previously cited in our literature review, the correlation between the Sequence V engine

**Table 21. Laboratory Oil Oxidation Test and Engine Test-Sequence IIIC
(Specification MIL-L-46152)**

Oil Sample	OC, ml	SEQUENCE IIIC		Ring Land Deposit
		“ 40 hours	“ 64 hours	
OS-37606	1317	111	173	8.1
OS-37709	885	126	4774	7.6
OS-37710	775	88	117	8.3
OS-37711	757	69	114	8.0
OS-37708	846	105	166	7.95
OS-37607	867	62	103	8.1
ERDA 1539	1002	18	ND	8.0
ERDA 1527	996	21	ND	7.5
AL-4597	425 (average)	981	TVTM	5.9
Reference Oil 70R	1422	> 600		
Reference Oil 70H	1281	> 2000		
(MIL-L-2104C) 6	765	385	TVTM	8.1
(MIL-L-2104C) 3	617	304	TVTM	7.0
(MIL-L-2104C) 9	294	9390	TVTM	6.9
Reference Oil LZ-1	1038	19.8	> 1500	ND
Reference Oil 70M	623	45	113	7.7
Reference Oil 71B	336	80	> 1000	ND
Reference Oil 73B	699	91	TVTM	7.9
Reference Oil 70G	1247	> 1000		ND
Reference Oil 70P	1028	> 1000		ND
GMR-9522	1296	> 1000		ND
GMR-9521	1416	> 1000		ND
GMR-9524	671	> 1000		ND
AL 5009	714	179	462	7.0
(MIL-L-46152) 1	658	83	1520	6.7
(MIL-L-46152) 2	954	50	4020	8.2
(MIL-L-46152) 9	1503	219	3860	7.6
(MIL-L-46152) 7	1220	66	269	6.7
(MIL-L-46152) 6	1014	63	TVTM	7.2
Reference Oil 75A	665	380	> 1000	7.4
Reference Oil 75B	1031	75	> 1000	6.5
Reference Oil 75C	690	120	266	7.9
Reference Oil 72A	622	352	> 1000	6.8
Reference Oil 73A	372	120	> 1000	7.6

ND: Not Determined.

TVTM: Too viscous to measure.

Table 22. Laboratory Oil Oxidation Test and Engine Test – Sequence VC
 (Specification MIL-L-46152 and MIL-L-2104C)

Oil Sample	OC, ml	Sequence VC		
		(Average)		
OS-37606	1317	8.0	8.3	9.6
OS-37709	885	7.9	8.2	9.6
OS-37710	775	8.2	8.3	9.6
OS-37711	757	8.1	8.6	9.6
OS-37708	846	7.9	7.9	9.6
OS-37607	867	7.9	8.4	9.6
ERDA 1539	1002	7.7	8.3	9.5
ERDA 1527	996	7.9	8.4	9.5
AL-4597	425 (average)	6.2	6.2	6.7
(MIL-L-2104C) 6	765	8.0	8.0	8.6
(MIL-L-2104C) 3	617	8.1	8.0	9.1
(MIL-L-2104C) 9	294	7.7	7.2	8.1
(MIL-L-2104C) 4	309	7.5	8.1	8.0
FREO 201-1	340	7.7	7.7	8.0
FREO 203	512	8.1	8.6	9.2
AL-5009	714	8.3	8.7	9.0
(MIL-L-46152) 1	658	8.5	8.2	9.1
(MIL-L-46152) 2	954	8.5	9.0	9.5
(MIL-L-46152) 9	1503	8.2	8.4	9.2
(MIL-L-46152) 7	1220	8.0	8.0	9.3
(MIL-L-46152) 6	1014	8.0	8.0	9.6

test and Forbes and Wood's bench test was feasible to derive because the latter reflected not only the effect of the engine oil but also of the fuel and combustion blow-by (98). No such fuel and combustion parameters were included in our laboratory oxidation method.

Eight samples of engine oils which were among those evaluated by this method were also tested in fleet tests in actual service (242) (247). The results are compared and presented in Table 23. Oxygen consumption varied from 129 to 1309 ml. Despite this difference in oxidation stability, all these engine oils operated satisfactorily in the field.

7. Conclusions from Oil Study.

- a. The new oxidation test is a reliable method for determining the oxidative stability of engine oil.
- b. No specific components or contaminants present in available samples of base stocks and engine oils were found to affect the oxidative stability of these oils.
- c. No linear correlation was found between oxidative stability of base stocks and that of engine oils formulated from these stocks.
- d. No linear correlation was found between oxidative stability of engine oil and oil parameters measured in single-cylinder engine, multicylinder engine and field tests.
- e. The reasons for the absence of correlations are:
 - (1) Performance of engine oil is not related to specific limiting characteristics of base oil.
 - (2) Oxidation is a minor factor in oil degradation during service in internal-combustion engines.
 - (3) Engine tests L-38 and Sequence VC evaluate several crankcase oil characteristics in addition to resistance to oxidation.
 - (4) Based upon published data (22), Sequence IIC engine test does not correlate with field performance and one of its characteristics - viscosity change reflects several phenomena.

Table 23. Laboratory Oil Oxidation Results and Field Performance

Oil Sample	OC, ml	Field Test	Results of Field Test
AL-6540 Formulated from Re-refined oil	963	San Diego Police Cruisers	Satisfactory performance
AL-6541 Formulated from Re-refined oil	901	San Diego Police Cruisers	Satisfactory performance
AL-6542 Formulated from Re-refined oil	1077	San Diego Police Cruisers	Satisfactory performance
AL-5009 Formulated from Synthetic Hydrocarbon	714	Letterkenny Fleet Test	Satisfactory performance
AL-5680 Formulated from Synthetic Ester	207	Letterkenny Fleet Test	Satisfactory performance
AL-5889 Formulated from Mineral oil	1309	Letterkenny Fleet Test	Satisfactory performance
AL-6095 Formulated from Mineral oil	293	Letterkenny Fleet Test	Satisfactory performance
AL-5075 Formulated from Synthetic Diester	129	Arctic Environment	Satisfactory performance

(5) In the field service, oil degradation depends upon several parameters such as oil characteristics, fuel, car, and driving conditions.

f. Decreased costs of qualification testing of engine oils will be achieved by eliminating the required Sequence III engine test from Military Specification MIL-L-46152.

VI. EXPERIMENTS

1. Oxidation of Gasolines and Their Constituents - Apparatus and Procedure.

The apparatus consists of a 300-ml stainless steel autoclave, equipped with a magnetic stirrer which can be regulated to a determined constant speed, an internal cooling coil, a temperature controller, a pressure recorder, and a stirred silicone oil bath installed on an electrically powered jack (see Figure 1).

In order to prevent corrosion and avoid catalytic effect of metals, the autoclave is fitted with Viton O-ring gaskets and the part of the stirrer inside the autoclave is made from a polycarbonate resin. The inside of the autoclave is coated with teflon. To improve the precision of the method and to be able to run unattended tests, the system has been partially automated. The system includes two timers for controlling the time of the reaction, heating, and cooling. At the end of the preset reaction time, the main timer shuts off the heating and stirring mechanisms and activates the jack which lowers the oil bath. At the same time, this timer turns on a second timer. The latter opens a solenoid valve which allows cold water from the faucet to circulate through the cooling coil inside the autoclave for a desired period of time.

The conditions of the oxidation test are: 50-ml sample in a glass liner, initial oxygen pressure of 100 lbf/in², reaction temperature of 100°C, internally measured, and stirring at 250 r/min. The duration of the reaction is 24 hours, measured from the time of raising the hot stirred oil bath, to the time of lowering it at the end of the experiment. No catalyst is used. At the beginning of the test, after placing the glass liner with the sample in the autoclave, oxygen is introduced until a pressure of 100 lbf/in² is attained. The gas in the autoclave is allowed to escape slowly in order to purge the air present. The purging is repeated three times. At the fourth time, the pressure of oxygen is set at 100 lbf/in². The pressure is recorded and observed for 10 minutes without stirring and then for 10 minutes with stirring to detect leaks. Afterwards, the heated and stirred silicon oil bath is raised. The main timer is set for 24 hours and the timer controlling the cooling period, for one hour. At the end of 24 hours, the heating and stirring is shut off, the oil bath is lowered, and the cold water is circulated through the cooling coil for 1 hour.

The volume of oxygen consumed is calculated from the pressure drop and converted to standard conditions (0°C and 760 mm hg pressure). The maximal volume of oxygen which can be consumed amounts to about 1600 ml. Next, the pressure is released slowly from the autoclave. The reaction product is separated into precipitate and liquid fraction by filtration. The liquid filtrate is weighed. The glass liner, the autoclave, and the stirrer are washed with hexane, and the washings are filtered through fritted glass filter containing the precipitate. The precipitate is dried and weighed. The dielectric constant and refractive index of the liquid filtrate and of the starting material are determined. The values of dielectric constant are obtained by measuring the capacitance of the liquids in a high-frequency oscilloscope at constant temperature. The oscilloscope is calibrated each time with four pure compounds of known dielectric constants. These compounds are: benzene, toluene, chlorobenzene, and carbon tetrachloride.

2. Oxidation of Oils. A system similar to the one used for gasolines was employed except the cooling coil which was omitted. More severe oxidation conditions were applied, a 50-ml oil sample was stirred at 350 r/min and 150°C for 48 hours. The procedure was similar to that employed for gasolines.

LITERATURE CITED

1. Department of the Army; Technical Manual TM-38-450, "Storage and Maintenance of Prepositioned Material Configured to Unit-Sets (POMCUS)," Chapter 5, Section VII (November 1971).
2. Department of the Army; Field Manual FM 10-70, "Inspecting and Testing Petroleum Products" (July 1976).
3. Department of Defense; Military Standardization Handbook MIL-HDBK-2001, "Quality Surveillance Handbook for Fuels, Lubricants, and Related Products," pp. 13 and 83 (November 1976); Military Specification MIL-G-3056D, "Gasoline, Automotive, Combat" (September 1975).
4. Department of the Army; Army Regulation No. 703-1, "Coal and Petroleum Products Management," Chapters 2 and 6 (September 1978).
5. J. N. Bowden, "Stability of MIL-G-3056-Type Gasoline," Ordnance Fuels and Lubricants Research Laboratory, Southwest Research Institute (November 1958).
6. M. E. LePera, "Investigation of the Autoxidation of Petroleum Fuels," AD 641270 (June 1966).
7. J. N. Bowden, "Storage Stability of Federal Specification Gasoline," U.S. Army Fuels and Lubricants Research Laboratory, Southwest Research Institute, AD 784282 (July 1974).
8. M. Kolobielski, "Determination of the Susceptibility of Gasoline to Oxidation by the Polarization Method," American Chemical Society, Division of Petroleum Chemistry, Preprints 21, No. 4, 898 (September 1976).
9. Coordinating Research Council; Phases I, II, and III; "Stationary Engine Tests Run by Southwest Research Institute," CRC Project No. CF-3-50; New York, NY (June 1957).
10. Coordinating Research Council; "Significance of Precipitate in MIL-G-3056 Motor Gasoline," CRC Project No. CG-1-58, New York, NY (February 1958).
11. Coordinating Research Council, Motor Vehicle-Fuel-Lubricant and Equipment Research Committee, "Induction System Deposit Effects on Engine Performance, ED Report No. 169 (August 1976).

12. Coordinating Research Council, Fuels and Engine Cleanliness Group; "Intake Manifold Deposit Engine Dynamometer Test Procedure - State-of-the-Art" Summary Report; 1973-1978 (December 1978).
13. Ford Motor Company; "Engine Engineering, A Presentation to SAE Fuel and Lubricants Subcommittee (Fuels) Regarding Fuel Cleanliness Characteristics," Dearborn, MI (February 1978).
14. "Annual Book of ASTM Standards," American Society for Testing and Materials, Part 23, Test D 525, Philadelphia, PA (1974).
15. E. G. Schwartz et al., "Storage Stability of Gasoline," Bureau of Mines, Bulletin 626 (1964).
16. E. G. Schwartz et al., "Storage Stability of Gasoline," Bureau of Mines, Bulletin 660 (1972).
17. "Significance of Tests for Petroleum Products," American Society for Testing and Materials; STP 7C, p. 48; Philadelphia, PA (1977).
18. W. R. Power, "The Invalid Induction Period," American Society for Testing and Materials; Bulletin 200, p. 58; Philadelphia, PA (1954).
19. R. O. Bender, in Symposium on Current Research on Motor Gasoline Which May Affect Future Specifications, American Society for Testing and Materials, STP 298, p. 63; Philadelphia, PA (1961).
20. A. C. Nixon, in "Autoxidation and Antioxidants," W. O. Lindberg, editor; Interscience Publishers, Vol. II, Chapter 17 - Autoxidation and Antioxidants of Petroleum, pp. 695-856, New York, NY (1962).
21. Military Specifications: MIL-I-2104 C, "Lubricating Oil, Internal Combustion Engine, Tactical Service" (20 November 1970); MIL-I-46152, "Lubricating Oil, Internal Combustion Engine, Administrative Service" (20 November 1970); MIL-I-21260 B, "Lubricating Oil, Internal Combustion Engine, Preservative and Break-In" (25 July 1972); MIL-I-46167, "Lubricating Oil, Internal Combustion Engine, Arctic" (15 February 1974).
22. "Multicylinder Test Sequences for Evaluating Automotive Engine Oils," Sequence HC, Sequence HHC, and Sequence VC, American Society for Testing and Materials, STP 315 G, Philadelphia, PA (1977).

23. Energy Policy and Conservation Act of 1975, U. S. Public Law 94-163; Conservation and Recovery Act of 1976, U. S. Public Law 94-580.
24. R. E. Albright et al., Ind. Eng. Chem. *41*, 897 (1949).
25. F. F. Farley and R. J. Greenshields, *ibid*; *41*, 902 (1949).
26. R. W. Watson and T. B. Tom, *ibid*, *41*, 918 (1949).
27. G. I. Kovalev, *Neftekhimiia* *18*, 584 (1978).
28. S. Benson, On Some Current Problems in Oxidation Kinetics, in National Bureau of Standards Publications 357, "The Mechanism of Pyrolysis, Oxidation and Burning of Organic Materials," p. 121 (1972).
29. R. H. Resenwald and J. R. Hoatson, Ind. Eng. Chem. *41*, 914 (1949).
30. C. J. Pedersen, *ibid*, *41*, 924 (1949).
31. R. P. Chisluk, Lubrication *54*, 85 (1968).
32. J. M. Dempster, ASTM Special Tech. Publ. *298*, 43 (1961).
33. E. T. Walters, Ind. Eng. Chem. *41*, 1723 (1949).
34. H. J. Scheule, ASTM Special Tech. Publ. *202*, 5 (1956).
35. J. L. Keller and F. S. Liggett, *ibid*, 21.
36. A. V. Carbal and J. Capowski, *ibid*, *47*.
37. A. C. Nixon, *ibid*, 56.
38. H. M. Smith, ASTM Special Tech. Publ. *304*, 62 (1961).
39. J. E. Ford et al., American Chemical Society, Division of Petroleum Chemistry, Preprints *2*, No. 1, 111 (1957).
40. F. R. Mayo, Conference on Oxidation of Hydrocarbons, Proceedings, p. 18, Bartlesville, OK (May 1961).

41. H. H. Zuidema, "The Performance of Lubricating Oils," Reinhold Publishing Corp.; New York, NY; pp. 68-76 (1959).
42. G. V. Dinneen and W. D. Bickel, Ind. Eng. Chem. 43, 1604 (1951).
43. R. B. Thompson, *ibid.*, 935.
44. R. V. Helm et al., American Chemical Society, Division Petroleum Chemistry, Preprints, p. A-17 (September 1957).
45. Y. G. Hendrickson, *ibid.*, p. 55 (April 1959).
46. A. C. Nixon and R. E. Thorpe, J. Chem. Eng. Data 7, 429 (1962).
47. R. A. Flinn et al., Hydroc. Proc. Petr. Refiner 42, 125 (1963).
48. C. F. Branderburg and D. R. Latham, J. Chem. Eng. Data 13, 391 (1968).
49. A. Ostwald and F. Noel, *ibid.*, 6, 294 (1961).
50. E. B. Smith and H. B. Jensen, Am. Chem. Soc., Div Petroleum Chem., Preprints, April 1965, p. C-123; J. Org. Chem. 32, 3330 (1967).
51. G. B. Quistael and D. A. Lightner, Chem. Comm., p. 1099 (1971).
52. J. W. Frankenfeld and W. F. Taylor, Exxon Res and Eng Co, Final Technical Report for the Department of the Navy, "Alternate Fuels Nitrogen Chemistry" (November 1977); Quarterly Progress Reports 1, 2, and 3 under contract N00019-78-C-0177 to the Department of the Navy, from February 1978 to October 1978.
53. R. B. Mesrobian and A. V. Tobolsky, in Autoxidation and Antioxidants, Vol I, p. 113, W. O. Lundbert, ed., Interscience Publishers, N.Y. (1962).
54. J. W. Davis, et al., U. S. Bureau of Mines, Report of Investigations No. 5798 (1961).
55. E. G. Schwartz and C. C. Ward, Soc. Autom. Eng. Report No. 650936 (1966).
56. E. Dimitroff and A. A. Johnston, Soc. Autom. Eng. Meeting, Houston, TX, Mechanism of Induction System Deposit (November 1966).

57. G. C. Bassler and J. R. Smith, Stanford Research Institute Final Report SU-1234, Menlo Park, CA (1961).
58. E. R. Mayo et al., *ibid*, The Chemistry of Fuel Deposits and Their Precursors (December 1972 and July 1973) (Report AD 754459).
59. E. R. Mayo and H. Richardson, *ibid* (December 1973).
60. W. F. Taylor and T. J. Wallace, Reports AD 489416 (August 1966) and AD 809288 (March 1967).
61. W. F. Taylor, Esso Res. Eng. Co., Development of High Stability Fuel, contract to U. S. Department of the Navy N00140-73-C-0547, (July 1973); Report AD A016592 (July 1975).
62. W. F. Taylor and T. J. Wallace, *Ind. Eng. Chem., Prod. Res. Dev.* **6**, No. 2, 58 (1967).
63. W. F. Taylor, *ibid*, 8, 375 (1969).
64. G. F. Bolshakov, AD 781164 (1972).
65. E. R. Mayo, *Ind. Eng. Chem.* **52**, 614 (1960).
66. E. R. Mayo, Amer. Chem. Soc., Div. Petroleum Chem., Preprints **17**, No. 3, A 39 (1972).
67. P. Polss, *ibid*, **17**, No. 3, B 111 (1972).
68. R. P. Baker and D. A. Yorke, *J. Chem. Educ.* **49**, 351 (1972).
69. R. A. Geisbrecht and T. E. Daubert, *Ind. Eng. Chem., Prod. Res. Dev.*, **15**, 115 (1976).
70. K. U. Ingold, *J. Inst. Petr.* **45**, 244 (1958).
71. J. A. Howard and K. U. Ingold, *Can. J. Chem.* **45**, 793 (1967).
72. K. Kanesaki and Y. Takenouchi, *Inter. Chem. Eng. (Japan)* **4**, 158 (1964).
73. Z. A. Sablina, Composition and Chemical Stability of Motor Fuels, ESTC-HF-23-1690-73, Translated from Russian Khimiya, Moscow 1972, p. 11 (1973).

74. Z. A. Sablina and A. A. Gureyev, Engine Fuel Additives, Translated from Russian, p. 70 (1977).
75. E. M. Goodger, Hydrocarbon Fuels, John Wiley and Sons, NY, p. 125 (1975).
76. J. N. Bowden, Stability Characteristics of Hydrocarbon Fuels from Alternate Sources, Final Report, U. S. Army Fuels and Lubricants Research Laboratory No. 114, under contract to U. S. Army MERADCOM, DAAK70-77-C-0115 (February 1979).
77. Yung-Yi Lin et al., Am. Chem. Soc., Div. Petr. Chem., Preprints 19, No. 5, 2 (1974).
78. R. N. Hazlett et al., U. S. Naval Research Laboratory Report No. 3844 (August 1978).
79. B. D. Vinyard and A.Y. Coran, Am. Chem. Soc. Div. Petro. Chem., Preprints 14, A-25 and A-35 (1969).
80. E. R. Braithwaite, Lubrication and Lubricants, Elsevier Publishing Co., N. Y., p. 140 (1967).
81. T. H. Rogers and B. H. Shoemaker, Ind. Eng. Chem., Anal. Ed. 6, 419 (1934).
82. R. W. Dornte, Ind. Eng. Chem. 28, 26, 863, 1342 (1936).
83. N. MacCoull et al., Society of Automotive Engineers, Transactions, 50, 338 (1942).
84. J. L. Bolland, Royal Society, Proceedings 186A, 218 (1946).
85. E. C. Hughes et al., Anal. Chem. 21, 737 (1949).
86. G. H. Beaven et al., J. Petr. Inst. 37, 25 (1951).
87. J. H. T. Brook et al., J. Inst. Petr. 39, 454 (1953).
88. S. B. Schexnailder, Air Res. Dev. Command, Technical Report 60-794, December 1960.
89. J. H. T. Brook, J. Inst. Petr. 48, 7 (1962).

90. G. M. Verley, U. S. Patent 3,044,860 (1962).
91. W. C. Hollyday and M. W. Munsell, U. S. Patent 3,076,791 (1963).
92. R. G. Moyer, U. S. Patent 3,143,877 (1964).
93. A. C. M. Wilson, J. Inst. Petr. 50, No. 482, 47 (1964); 59, No. 566, 45 (1973).
94. A. C. M. Wilson, Lubrication Engineering, p. 59 (February 1976).
95. J. R. Barcelo and C. Otero, J. Inst. Petr. 50, 15 (1964).
96. E. A. Oberright et al., ASLE TRANS. 7, 64 (1964).
97. E. E. Klaus et al., Report AD 837221 (1968).
98. E. S. Forbes and J. M. Wood, Am. Chem. Soc., Div. Petr. Chem., Preprints 13, No. 2, B 105 (1968).
99. B. D. Boss and R. N. Hazlett, Naval Res. Lab., Report No. 6788 (December 1968); Ind. Eng. Chem. Prod. Res. Develop. 14, 135 (1975).
100. A. L. Williams, Am. Chem. Soc., Div. Petr. Chem., Preprints 14, A7 (1969).
101. T. S. Chao et al., SAE 700890 (1970).
102. G. O. Dotterer, Rev. Sc. Instruments, 42, 471 (1971).
103. E. F. Pierce, Naval Air Propulsion Test Center, Report NAPTC-AED-1960 (1971).
104. A. J. Burn and G. Greig, J. Inst. Petr. 58, 346 (1972).
105. R. Cecil, J. Inst. Petr., 59, 201 (1973).
106. R. R. Kuhn, Am. Chem. Soc., Div. Petr. Chem., Preprints, 18, 694 (1973).
107. E. E. Klaus et al., Report AD A009515 (1974).
108. F. Noel, J. Inst. Petr. 57, 354, (1971).
109. F. Noel and G. E. Cranton, Anal. Calorimetry 3, 305 (1974).

110. R. L. Blaine, NLGI Spokesman 40, 94 (1976).
111. H. Ravner and P. J. Sniegoski, Naval Res. Lab. Memorandum Report 3644 (November 1977).
112. E. E. Klaus and E. J. Tewksbury, Report AD B026756 (1977).
113. L. R. Mahoney et al., Ind. Eng. Chem. Prod. Res. Develop. 17, 250 (1978).
114. A. Vranos, ibid, 296 (1978).
115. G. H. von Fuchs et al., Am. Soc. for Testing and Materials Bulletin 186, 43 (1952).
116. G. H. von Fuchs, Lubricating Engineering, p. 22 (January 1960).
117. C. J. Linch, U. S. Army Weapons Command, Technical Report 68-897 (April 1968).
118. J. S. Elliott et al., J. Inst. Petr. 55, 219 (1969).
119. M. D. Klinkhamer, Liquid Lubricants, David W. Taylor Naval Ship R&D Center, Project Brief (January 1978).
120. Anonymous, Lubrication, 49, 157 (1963).
121. J. A. McLain, Lubrication Engineering, 24, 254 (1968).
122. R. W. Jack, Lubrication 55, 77 (1969).
123. K. D. Relyea, Lubrication 59, 49 (1973).
124. A. N. Smith, Lubrication Engineering 32, 66 (1976).
125. W. M. Cummings, Lubrication 63, 1 (1977).
126. G. J. Schilling and G. S. Bright, Lubrication 63, 13 (1977).
127. O. D. Vail, ibid, 25.
128. C. H. Young, ibid, 37.

129. J. H. Taylor, Petroleum Review 32, 38 (May 1978).
130. Federal Test Method Standard No. 791 B, Method 5307, Corrosiveness and Oxidation Stability of Aircraft Turbine Engine Lubricants (20 June 1974).
131. Ibid, Method 5308.6, Corrosiveness and Oxidation Stability of Light Oils (15 January 1969).
132. Annual Book of ASTM Standards, American Society for Testing and Materials, Philadelphia, PA (1975); Part 23, Tests D893, D943 and D1313; Part 24, Tests D2272 and D2893; Part 25, Test D3241; Part 40, Tests D1934, D2112 and D2440.
133. Institute of Petroleum Standards for Petroleum and its Products, Part I, Tests IP 48/67, IP 157/64, IP 229/73, IP 280/73, IP 306/75, IP 307/75, and IP 328/76; 35th edition, Applied Science Publishers LTD, Great Britain (1976).
134. Federal Test Method Standard No. 791 B, Method 340.3, Performance of Engine Lubricating Oils Under Medium Speed Supercharged Conditions with High-Sulfur Content; Method 341.3, Performance of Engine Lubricating Oils Under High Speed Supercharged Conditions; Method 346.2, Performance of Engine Lubricating Oils Under High Temperature Medium Supercharged Conditions; Method 348.2, Performance of Crankcase Lubricating Oils in CLR Engine; Method 354, Performance of Arctic Lubricating Oils in a Two-cycle Diesel Engine Under Steady State, Turbo-Supercharged Conditions; Method 3405.2, Oxidation of Crankcase Lubricating Oils in CLR Engine (15 January 1969, 8 March 1972, and 20 June 1974).
135. Single-Cylinder Engine Tests, American Society for Testing and Materials, STP 509; Test FTM 3405.1 (Oxidation, CRC L-38); Test FTM 348 (Low Temperature Deposits, CRC LTD); FTM 340.2 (Diesel Test, Caterpillar Test 1-D); FTM 346 (Diesel Test, Caterpillar Test 1-H); FTM Test 341.2 (Diesel Test; Caterpillar Test 1-G).
136. 1977 SAE Handbook, Recommended Practices; SAE J 183a, Engine Oil Performance and Engine Service Classification; Information Report J 304 b, Engine Oil Tests; SAE J 357, Information Report, Physical and Chemical Properties of Engine Oils; Society of Automotive Engineers, Inc., Warrendale, PA.

137. C. F. Konitz, Lubrication 58, 1 (1972).
138. Coordinating European Council (CEC) - Lubricants Technical Committee's Engine Test Methods for European Cars. A. Marciante and F. Wolff in Performance Testing of Lubricants for Automotive Engines and Transmissions, C. F. McCue et al., Editors, Applied Science Publishers, LTD, Great Britain, p. 7 (1974).
139. W. A. Snook, Lubrication 54, 97 (1968).
140. N. E. Gallopoulos, SAE Paper 700506 (May 1970).
141. R. H. Kabel, SAE Paper 700507 (May 1970).
142. D. C. Bardy and P. A. Asseff, SAE Paper 700508 (May 1970).
143. L. J. Allman et al., SAE Paper 700510 (May 1970).
144. Shoich Furuhama and Masaru Hiruma, Lubricating Engineering 34, 665 (1978).
145. J. V. D. Wilson et al., SAE Paper 720688 (August 1972).
146. J. A. Spearot, Am. Chem. Soc., Div. Petr. Chem., Preprints 19, 598 (1974).
147. Am. Soc. Testing and Materials, Data Series Publication DS 49, Shear Stability of Multigrade Crankcase Oil (1973).
148. Am. Soc. Testing and Materials Publication DS 49 S-1 (1974).
149. W. C. Edminstein et al., SAE Paper 700509 (May 1970).
150. M. Kolobielski, Report AD 779406 (April 1974).
151. E. Wedepohl and W. J. Bartz, Motortech., Z. 38, 319 (1977).
152. Society of Automotive Engineers, Fuels and Lubricants Technical Committee, Task Force, Final Report on Used Oil Viscosity Survey (November 1978).
153. W. Wunderlich and H. Jost, SAE Paper 780372 (1978).
154. W. J. Bartz and D. Wissussek, in Performance Testing of Lubricants for Automotive Engines and Transmissions. C. F. McCue et al., editors, Applied Science Publishers, LTD, Great Britain, p. 505 (1974).

155. T. F. Lonstrup and J. Sequeira, *ibid.*, p. 475.
156. A. D. Bramhall and B. Wright, *ibid.*, p. 487.
157. R. E. Paggi and R. E. Andrus, SAE Paper 700511 (1970).
158. G. H. Denison, Jr., and J. Q. Clayton, SAE Transactions 53, 264 (1945).
159. K. A. Frassa et al., SAE Paper 951 D (1965).
160. A. Bondi, *Physical Chemistry of Lubricating Oils*, Reinhold Publishing Corp., N.Y. (1951).
161. A. Bondi et al., *Lubrication Engineering* 12, 267 (1956).
162. H. H. Zuidema, "The Performance of Lubricating Oils," Reinhold Publishing Corp., New York, p. 118 (1959).
163. K. A. Kobe and J. J. McKetta, *Advances in Petroleum Chemistry and Refining*, vol. 7, Interscience Publishers, New York (1963).
164. G. J. Parsons, *J. Inst. Petrol.* 55, 256 (1969).
165. K. L. Kreuz, *Lubrication* 56, 77 (1970).
166. Heavy-Duty Oils for High-Speed High-Power Diesel Engine, Federal Republic of Germany, Navy Test Center 71 Kiel, Report No. 5316050677 (March 1977).
167. J. Geyer, *Am. Chem. Soc. Div. Petrol. Chem., Preprints*, 14, A15 (1969).
168. F. G. Rounds, SAE Report 770829 (1977).
169. J. B. Matthews, *J. Inst. Petr.* 39, 430 (1953).
170. H. C. Evans and J. B. Matthews, *J. Inst. Petr.* 39, 463 (1953).
171. J. Hughes and J. B. Matthews, *J. Inst. Petr.* 39, 463 (1953).
172. K. L. Kreuz and R. F. Love, *Am. Chem. Soc., Div. Petr. Chem., Preprints*, 14, A47 (1969).

173. T. M. Sugden, Chemistry and Industry, 7 February 1970, p. 174.
174. R. D. Novoded et al., NEFTEPERERAB. NEFTEKHIM. 9, 32 (1973).
175. E. E. Klaus, Am. Soc. Mech. Engineers, Conference in New York, paper 63-MD-27 (May 1963).
176. H. A. Hartung, Am. Soc. Mech. Engineers, Transactions, p. 883 (December 1964).
177. Anonymous, Lubrication 51, 45 (1965).
178. V. Hopkins, Am. Soc. Aut. Eng., J. Basic Engin., p. 613 (September 1966).
179. A. R. Lansdown, 1972 Symposium on Interdisciplinary Approach to Liquid Lubricant Technology, NASA, Washington, DC, p. 1 (1973).
180. F. G. Rounds and N. A. Hunstad, ibid, p. 44.
181. T. Salomon, ibid, p. 48.
182. N. W. Furry, ibid, p. 57.
183. E. Klaus, ibid, p. 81.
184. T. Salomon, ibid, p. 85 and 123.
185. J. K. Appledoorn, ibid, p. 90.
186. C. V. Smalheer, ibid, p. 433.
187. R. S. Spindt et al., SAE Journal, April 1956, p. 120.
188. R. G. Mastin and L. J. Gorry, Lubr. Engin. 18, 517 (1962).
189. K. L. Kreuz, Lubrication 55, 53 (1969).
190. C. Staley, 1972 Symposium on Interdisciplinary Approach to Liquid Lubricant Technology, NASA, Washington, DC, p. 461 (1973).
191. Harumichi Watanabe and Chikara Kobayashi, Lubr. Engin. 34, 421 (1977).

192. Yun-Chung Sun, Am. Chem. Soc. Div. Petr. Chem., Preprints, 19, No. 1, 76 (1974).
193. N. C. C. Li and T. D. Terry, J. Am. Chem. Soc., 70, 344 (1948).
194. V. I. Minkin et al., "Dipole Moments in Organic Chemistry," Plenum Press, New York, NY (1970).
195. R. J. W. LeFevre, "Dipole Moments," Methuen and Co., London, p. 87 (1953).
196. R. Irving and C. N. Thompson, Chem. and Ind., p. 975 (4 October 1952).
197. R. W. Walker, "A Critical Survey of Rate Constants for Reactions in Gas-phase Hydrocarbon Oxidation, in Reaction Kinetics," Volume 1, p. 161, The Chemical Society, London (1975).
198. E. S. Huyser, "Free-Radical Chain Reactions," Wiley-Interscience, New York, p. 307 (1970).
199. D. J. Hucknall, "Selective Oxidation of Hydrocarbons," Academic Press, New York, p. 113 (1974).
200. W. L. Nelson, "Petroleum Refinery Engineering," McGraw-Hill Book Co., New York, NY (1969).
201. C. H. Robinson, The Effect of Gasoline Additives on Fuel Economy, In Fuel Economy of the Gasoline Engine; D. R. Blackmore and A. Thomas, Editors, John Wiley and Sons; New York, NY; p. 80 (1977).
202. J. W. Andrew et al., Hydroc. Proc., p. 69 (May 1975).
203. P. L. Dartwell and K. Campbell, Oil and Gas J., p. 205 (13 November 1978).
204. R. F. Burtner and W. E. Morris, SAE Report 780949 (1978).
205. "Knocking Characteristics of Pure Hydrocarbons," American Society for Testing and Materials, STP 225, Philadelphia, PA (1958).
206. K. C. Salooja, Combustion and Flame 12, 401 and 597 (1968).
207. D. J. McEwen, American Chemical Society, Division of Petroleum Chemistry, Preprints, vol. 12, No. 2, B-41 (1967).

208. W. N. Sanders and J. B. Maynard, *Anal. Chem.* **40**, 527 (1968).
209. J. B. Maynard and W. N. Sanders, *J. Air Poll. Control Assoc.* **19**, 505 (1969).
210. R. F. Burtner, Am. Soc. for Testing and Materials, STP 487 (1970).
211. J. N. Bowden, "Status of Unleaded and Low-lead gasoline Composition," US Army Fuels and Lubricants Research Laboratory, Report AD 747421, (1972).
212. J. N. Bowden, "Trends in Properties of Unleaded Gasoline," US Army Fuels and Lubricants Research Laboratory, Report ADA008407 (1975).
213. R. Cassidy and C. Schuerch, *J. Chem. Educ.* **53**, 51 (1976).
214. DuPont, Motor Gasoline Properties, Summer 1976, Technical Brief 7704 (March 1977).
215. DuPont, Road Octane Survey, Summer 1978.
216. (a) DuPont, Road Octane Survey, 1978-79 Winter.
(b) Petroleum Chemicals, 1978 Technical Conference.
217. Anonymous, *Chemical Engineering*, p. 101 (23 October 1978).
218. Anonymous, *Chemical and Engineering News*, p. 4, (16 April 1979).
219. G. H. Hobson and W. Pohl, "Modern Petroleum Technology," Applied Science Publishers, Great Britain, (1973).
220. Anonymous, *Chemical Week*, p. 49, (16 November 1977).
221. D. G. Reynolds, *The Oil and Gas Journal*, p. 68 (12 December 1977).
222. Anonymous, *Chemical Engineering*, p. 93 (23 October 1978).
223. P. G. Bercik et al., *Ind. Eng. Chem. Prod. Res. Develop.* **17**, No. 3 214 (1978).
224. Masaki Sato, "Hydrocarbon Processing," p. 141 (May 1973).
225. B. Lohr and H. Dittmann, *The Oil and Gas Journal*, p. 78 (18 July 1977).
226. B. Lohr et al., *ibid.*, p. 82 (26 March 1979).

227. T. C. Ponder, *Hydrocarbon Processing*, p. 111 (December 1977).
228. A. G. Goosens et al., *ibid.*, p. 227 (September 1978).
229. Anonymous, *Chemical Week*, p. 44 (21 May 1975).
230. K. A. Boltel and S. T. Griffith, *Motor Gasoline and Vaporizing Oil*, Chapter 5 in *Criteria for Quality of Petroleum Products*, J. P. Allison, editor, John Wiley and Sons, New York, NY (1973).
231. F. H. Adams, *Hydrocarbon Processing*, p. 113 (October 1973).
232. D. P. Satchell and B. L. Crynes, *The Oil and Gas Journal*, p. 123 (1 December 1975).
233. Anonymous, *ibid.*, p. 43 (28 March 1977).
234. J. D. Chase and H. J. Woods, *ibid.*, p. 149 (9 April 1979).
235. Anonymous, *Chemical Week*, p. 39 (14 June 1978).
236. Anonymous, *ibid.*, p. 41 (26 July 1978).
237. J. S. Magee and R. E. Ritter, *Am. Chem. Soc., Div. Petrol. Chem. Preprints*, 23, No. 3, 1057 (September 1978).
238. C. P. Carter, *Hydroc. Process.*, p. 237 (September 1978).
239. J. W. Ward and S. A. Quader, *Hydrocracking and Hydrotreating*, ACS Symposium Series 20, Am. Chem. Soc., Washington, DC (1975).
240. G. F. Addison et al., *The Oil and Gas J.*, p. 59 (7 July 1975).
241. E. Fehr et al., Am. Petr. Institute Refining Dept., *Proceedings*, p. 459 (May 1978).
242. E. A. Frane and T. C. Bowen, US Army Environmental Protection Agency Refined Engine Oil Program, US Army Fuels and Lubricants Research Laboratory Report No. 98 (May 1978).
243. R. P. Bryer, *Lubrication Engin.*, 28, 311 (1972).

244. P. A. Asseff, ASLE Transactions, 19, No. 2, 93 (1976).
245. L. P. Sands, Comments on Additive Response to Different Base Oils, in Measurements and Standards for Recycled Oil, NBS Special Publication 488, p. 61 (August 1977).
246. J. W. Reynolds et al., Engine Sequence Testing of Re-refined Lubricating Oils, Energy Research and Development Administration, Bartlesville Energy Research Center, BERC OP-76-29 (October 1976); Hydrocarbon Processing, p. 128 (September 1977).
247. J. D. Tosh and J. A. Russell, "Evaluation of Environmental and Economic Benefits Through Use of Synthetic Motor Oils," Report ADA046277 (September 1977).

LIST OF SYMBOLS

Symbol	General Meaning
ϵ	Dielectric Constant
n	Number of Tests
n_D	Refractive Index Observed with Visible Light
ND	Not Determined
OC	Oxygen Consumption
P	Probability Level
PI	Polarization Index
$PI = \epsilon - n_D^2$	
PI_{Δ}	Polarization Index Differential
$PI_{\Delta} = PI_{\text{oxidized sample}} - PI_{\text{initial sample}}$	
R	Correlation Coefficient
RON	Research Octane Number
r/min	Revolutions per Minute
S	Standard Deviation or Standard Error of Estimate
S/\bar{X}	Coefficient of Variations
TVTM	Too Viscous to Measure
V	Coefficient of Variations
\bar{X}	Mean

DISTRIBUTION FOR MERADCOM REPORT 2296

No. Copies	Addressee	No. Copies	Addressee
1	HQ, Dept of the Army ATTN: DAEO-TSE	1	HQ, 172d Infantry Brigade (Alaska) ATTN: AFZT-DI-L
1	ATTN: DAMA-CSS-P (Dr. Bryant) Washington, DC 20310		Directorate of Industrial Operations APO Seattle 98749
	CDR US Army Materiel Dev & Readiness Command	1	CDR US Army General Material & Petroleum Activity
1	ATTN: DRCLDC (Mr. Zentner)	1	ATTN: STSGP-FT
1	ATTN: DRCMM-SP 5001 Eisenhower Ave Alexandria, VA 22333	1	ATTN: STSGP-PF New Cumberland Army Depot New Cumberland, PA 17070
	CDR US Army Tank-Automotive Res & Dev Com	1	CDR US Army TAA
1	ATTN: DRDLA-R	1	ATTN: DAEO-TFP (UIC Hester)
1	ATTN: DRDLA-NS (Dr. Petrick)		New Cumberland Army Depot, New Cumberland, PA 17070
1	ATTN: DRDLA-J Warren, MI 48090	1	CDR US Army General Material & Petroleum Activity
	CDR US Army Tank-Automotive Materiel Readiness Com	1	ATTN: STSGP-PW Sharpe Army Depot Lathrop, CA 95330
1	ATTN: DRSTA-G		CDR US Army Foreign Science & Tech Center
1	ATTN: DRSTA-M	1	ATTN: DRXSL-MTC Federal Bldg Charlottesville, VA 22901
1	ATTN: DRSTA-GBP (Mr. McCartney) Warren, MI 48090	1	CDR DARCOM Materiel Readiness Support Activity (MRSA)
	Director US Army Materiel Systems Analysis Agency	1	ATTN: DRXMD-MS Lexington, KY 40511
1	ATTN: DRXSY-CM (Mr. Woerner)		HQ, US Army Test & Eval Com
1	ATTN: DRXSY-S Aberdeen Proving Ground, MD 21005		ATTN: DRSTL-TO-O Aberdeen Proving Ground, MD 21005
	CDR US Army Applied Tech Lab	1	
1	ATTN: DAVDI-ATL-ATP (Mr. Morrow)		
1	ATTN: DAVDI-ATI Fort Eustis, VA 23604		

No. Copies	Addressee	No. Copies	Addressee
1	HQ, US Army Armament Research & Dev Com ATTN: DRDAR-LCA-OO	1	CDR US Army Research & Stdzn Group (Europe) ATTN: DRXSN-F-RA Box 65 FPO NY 09510
1	ATTN: DRDAR-TSF-S Dover, NJ 07801		
2	HQ, US Army Troop Support & Aviation Materiel Readiness Com ATTN: DRSTS-MFG	1	HQ, US Army Aviation Research & Dev Com
1	ATTN: DRCPO-PDF (Ltc Foster) 4300 Goodfellow Blvd St Louis, MO 63120	1	ATTN: DRDAV-D (Mr. Crawford)
1	Department of the Army Construction Engineering Res Lab ATTN: CERI-FM PO Box 4005 Champaign, IL 61820	1	ATTN: DRDAV-N (Mr. Borgman)
1	ATTN: DRDAV-E (Mr. Long) PO Box 209 St Louis, MO 63166		
1	HQ US Army Training & Doctrine Com ATTN: ATCD (MAJ Harvey) Fort Monroe, VA 23651	1	CDR US Army Forces Command ATTN: AFIG-RFG (Mr. Hammerstrom) Fort McPherson, GA 30330
1	Director US Army Research & Tech Labs (AVRADCOM) Propulsion Laboratory ATTN: DAVID-PL-D (Mr. Acuno) 21000 Brookpark Road Cleveland, OH 44135	1	CDR US Army Aberdeen Proving Grd ATTN: STAP-MI Aberdeen Proving Ground, MD 21005
1	CDR US Army Natick Research & Development Com ATTN: DRDNA-YEP (Dr. Kaplan) Natick, MA 01760	1	CDR US Army Yuma Proving Ground ATTN: STEYP-MI Yuma, AZ 85364
1	CDR US Army Cold Region Test Ctr ATTN: SECRC TA (Mr. Haslem) APO Seattle 98133	1	Michigan Army Missile Plant Ofc of Proj Mgr, XM-1 Tank Sys ATTN: DRCPM-GCM-S Warren, MI 48090
		1	Michigan Army Missile Plant Proj Mgr, Fighting Vehicle Sys ATTN: DRCPM-FVS-SI Warren, MI 48090
		1	Proj Mgr, M60 Tank Development ATTN: DRCPM-M60-IDT Warren, MI 48090

No. Copies	Addressee	No. Copies	Addressee
1	Prod Mgr, M113/M113A1 Family of Vehicles ATTN: DRCPM-M113 Warren, MI 48090	1	DIR US Army Research & Tech Lab Advanced Systems Rsch Ofc (ATTN: Mr. D. Wilsted) Ames Rsch Ctr Moffit Field, CA 94035
1	Proj Mgr, Mobile Elec Power ATTN: DRCPM-MEP-TM 7500 Backlick Road Springfield, VA 22150	1	CDR US Army Transportation School ATTN: ATSP-CD-MS Fort Eustis, VA 23604
1	Ofc of Proj Mgr, Improved Tow Vehicle US Army Tank-Automotive Rsch & Dev Com ATTN: DRCPM-ITV-T Warren, MI 48090	1	CDR US Army Quartermaster School ATTN: ATSM-CD-M
1	CDR US Army Europe & Seventh Army ATTN: AEAGC-FMD APO NY 09403	1	ATTN: ATSM-CTD-MS (MAJ Brewster)
1	Proj Mgr, Patriot Proj Ofc ATTN: DRCPM-MD-T-G US Army DARCOM Restone Arsenal, AL 35809	1	ATTN: ATSM-TNG-PT (LTC Volpe) Fort Lee, VA 23801
1	CDR Theater Army Material Mgmt Center (200th) Directorate for Petrol Mgmt ATTN: AEAGD-MM-PT-Q (Mr. Pinzola) Zweibrucken APO NY 09052	1	HQ, US Army Armor School ATTN: ATSB-TD Fort Knox, KY 40121
1	CDR US Army Research Ofc ATTN: DRXRO-EG (Mr. Murray) ATTN: DRXRO-CB (Dr. Ghirardelli) PO Box 12211 Rsch Triangle Park, NC 27709	1	CDR US Army Logistics Center ATTN: ATCL-MS (Mr. A. Marshall) Fort Lee, VA 23801
1		1	CDR US Army Field Artillery School ATTN: ATSF-CD Fort Sill, OK 73503
1		1	CDR US Army Ordnance Center & School ATTN: ATSL-CTD-MS Aberdeen Proving Ground, MD 21005

No. Copies	Addressee	No. Copies	Addressee
1	CDR US Army Engineer School ATTN: ATSE-CDM Fort Belvoir, VA 22060	2	Tech Library, DRDME-WC
1	CDR US Army Infantry School ATTN: ATSH-CD-MS-M Fort Benning, GA 31905	1	Programs & Anal Direc, DRDME-U
	MERADCOM	1	Pub Affairs Ofc, DRDME-I
1	Commander, DRDME-Z Technical Dir, DRDME-ZT Assoc Tech Dir/R&D, DRDME-ZN Assoc Tech Dir/Engrg & Acq, DRDME-ZE Spec Asst/Matl Asmt, DRDME-ZG Spec Asst/Ses & Tech, DRDME-ZK CIRCULATE	1	CDR US Air Force Wright Aeronautical Lab ATTN: AFWAL/POSF (Mr. Churchill)
1	Chief, Ctrmine Lab, DRDME-N Chief, Engy & Wtr Res Lab, DRDME-G Chief, Elec Pwr Lab, DRDME-E Chief, Cam & Topo Lab, DRDME-R Chief, Mar & Br Lab, DRDME-M Chief, Mech & Constr Eqpt Lab, DRDME-H Chief, Ctr Intrus Lab, DRDME-X Chief, Matl Tech Lab, DRDME-V Director, Product A&T Directorate, DRDME-T CIRCULATE	1	ATTN: AFWAL/POSF (Mr. Jones) ATTN: AFWAL/POSF (Mr. Beane) Wright-Patterson Air Force Base, OH 45433
1	CDR USAF San Antonio Air Logistics Center ATTN: SAALC/SFQ (Mr. Makris) ATTN: SAALC/MMPRR (Mr. Elliot) Kelly Air Force Base, TX 78241		
5	Engy & Water Res Lab, DRDME-G	1	CDR US Air Force Wright Aeronautical Lab ATTN: AFWAL/MLSE
30	Fuels & Lubs Div, DRDME-GL	1	ATTN: AFWAL/MXE MLXE Wright-Patterson Air Force Base, OH 45433
30	M. Kolobielski Grp, DRDME-GL	1	CDR USAF Warner Robins Air Log Ctr ATTN: WR-ALC/MMIRAB-1 (Mr. Graham)
3	Tech Reports Ofc, DRDME-WP	1	Robins Air Force Base, GA 31098
3	Security Ofc (for liaison officers), DRDME-S	1	CDR Naval Air Propulsion Ctr ATTN: PI-7 Trenton, NJ 08628

No. Copies	Addressee	No. Copies	Addressee
1	CDR Naval Ship Engineering Ctr Code 6101F (Mr. R. Layne) Washington, DC 20362	1	CDR Naval Facilities Engr Ctr ATTN: Code 1032B (Mr. B. Burris) ATTN: Code 120B (Mr. Buschelman) 200 Stovall St Alexandria, VA 22322
1	CDR David Taylor Naval Ship Research & Develop Ctr Code: 2830 (Mr. G. Bosmajian)	1	Chief of Naval Research ATTN: Code 473 (Dr. R. Miller) Arlington, VA 22217
1	Code: 2831 Annapolis, MD 21402	1	Department of Defense ATTN: DASA (MRA&L)-ES Washington, DC 20301
1	Joint Oil Analysis Program – Technical Support Ctr Bldg 780 Naval Air Station Pensacola, FL 32508	1	CDR Naval Air Engr Center ATTN: Code 92727 (Mr. O'Donnell) Lakehurst, NJ 08733
1	Department of the Navy HQ, US Marine Corps ATTN: LMM (MAJ Griggs)	1	Other Government Agencies
1	ATTN: LPP (MAJ Sanberg) Washington, DC 20380	1	Bartlesville Energy Tech Ctr ATTN: Mr. C. J. Thompson ATTN: Dr. D. W. Brinkman Box B98 Bartlesville, OK 74003
1	CDR Naval Air Systems Command ATTN: Code 52032E (Mr. Weinburg)	1	National Bureau of Standards Bldg 221, Room B326 ATTN: Mr. D. A. Becker
1	ATTN: Code 53645 (Mr. Collegeman) Washington, DC 20361	1	ATTN: Dr. J. J. Comeford ATTN: Dr. S Hsu Washington, DC 20234
1	CDR Naval Air Development Ctr ATTN: Code 60612 (Mr. L. Stallings) Warminster, PA 18974	1	Others
1	CDR Naval Research Lab ATTN: Code 6170 (Mr. H. Ravner)	1	Professor Raymond R. Fox School of Engineering and Applied Science The George Washington Univ Washington, DC 20052
1	ATTN: Code 6180 Washington, DC 20375		

No. Copies	Addressee	No. Copies	Addressee
3	Mr. Roy D. Quillian, Jr. Director US Army Fuels and Lubricants Research Laboratory Southwest Research Institute PO Drawer 28510 San Antonio, TX 78228	1	Mr. A. A. Krawetz Phoenix Chemical Lab 3953 Shakespeare Ave. Chicago, IL 60647
1	Mr. Fred McCaleb Rt 2, Box 50C Fayette, Alabama 35555	1	Research Labs General Motors Corporation ATTN: Mr. N. E. Galopoulos ATTN: Mr. R. H. Kabel 12 Mile and Mound Roads Warren, MI 48090
1	Mr. P. L. Rigner National Research Council Div of Mechanical Engineering Ottawa, Ontario K1A OR 6 Canada	1	Mr. P. A. Asseff Lubrizol Corporation 29400 Lakeland Blvd Wickliffe, OH 44092
1	Mr. R. F. Pedall Motor Oil Refining Company 7601 West 47th Street McCook, IL 60525	1	Mr. T. S. Chao Atlantic Richfield Company Engine Oils 400 East Sibley Boulevard Harvey, IL 60426
1	Mr. K. A. Frassa Mobil Oil Corporation 150 E 42nd Street New York, NY 10017	1	Dr. S. Korcek Ford Motor Company PO Box 2053 Dearborn, MI 48121
1	Mr. J. W. Swain, Jr. 40 Denton Road Wellesbey, MA 02181		
1	Dr. T. W. Selby Savant, Inc. 234 E. Larkin Street Midland, MI 48640		
1	Dr. T. H. Webb The Standard Oil Company 3092 Broadway Avenue Cleveland, OH 44115		
1	Mr. A. N. Smith General Electric Company Building 53 - Room 312 Schenectady, NY 12345		

**DAU
ILM**